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Introduction

class="introduction"

- Chemistry in Context
- Phases and Classification of Matter
- Physical and Chemical Properties
- Measurements
- Measurement Uncertainty, Accuracy, and Precision
- Mathematical Treatment of Measurement Results
- Module for Testing Functions of Various Items to See How They Generate in the PDF

Chemical
substances and
processes are
essential for our
existence,
providing
sustenance,
keeping us clean
and healthy,
fabricating
electronic devices,
enabling
transportation, and
much more.

(credit “left”:
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Your alarm goes off and, after hitting “snooze” once or twice, you pry yourself out of bed. You make a cup of coffee to help you get going, and then you shower, get dressed, eat breakfast, and check your phone for messages. On your way to school, you stop to fill your car’s gas tank, almost making you late for the first day of chemistry class. As you find a seat in the classroom, you read the question projected on the screen: “Welcome to class! Why should we study chemistry?”

Do you have an answer? You may be studying chemistry because it fulfills an academic requirement, but if you consider your daily activities, you might find chemistry interesting for other reasons. Most everything you do and encounter during your day involves chemistry. Making coffee, cooking eggs, and toasting bread involve chemistry. The products you use—like soap and shampoo, the fabrics you wear, the electronics that keep you connected to your world, the gasoline that propels your car—all of these and more involve chemical substances and processes. Whether you are aware or not, chemistry is part of your everyday world. In this course, you

will learn many of the essential principles underlying the chemistry of modern-day life.

Chemistry in Context

By the end of this module, you will be able to:

- Outline the historical development of chemistry
- Provide examples of the importance of chemistry in everyday life
- Describe the scientific method
- Differentiate among hypotheses, theories, and laws
- Provide examples illustrating macroscopic, microscopic, and symbolic domains

Throughout human history, people have tried to convert matter into more useful forms. Our Stone Age ancestors chipped pieces of flint into useful tools and carved wood into statues and toys. These endeavors involved changing the shape of a substance without changing the substance itself. But as our knowledge increased, humans began to change the composition of the substances as well—clay was converted into pottery, hides were cured to make garments, copper ores were transformed into copper tools and weapons, and grain was made into bread.

Humans began to practice chemistry when they learned to control fire and use it to cook, make pottery, and smelt metals. Subsequently, they began to separate and use specific components of matter. A variety of drugs such as aloe, myrrh, and opium were isolated from plants. Dyes, such as indigo and Tyrian purple, were extracted from plant and animal matter. Metals were combined to form alloys—for example, copper and tin were mixed together to make bronze—and more elaborate smelting techniques produced iron. Alkalis were extracted from ashes, and soaps were prepared by combining these alkalis with fats. Alcohol was produced by fermentation and purified by distillation.

Attempts to understand the behavior of matter extend back for more than 2500 years. As early as the sixth century BC, Greek philosophers discussed a system in which water was the basis of all things. You may have heard of the Greek postulate that matter consists of four elements: earth, air, fire, and water. Subsequently, an amalgamation of chemical technologies and philosophical speculations were spread from Egypt, China, and the eastern Mediterranean by alchemists, who endeavored to transform “base metals”

such as lead into “noble metals” like gold, and to create elixirs to cure disease and extend life ([link](#)).

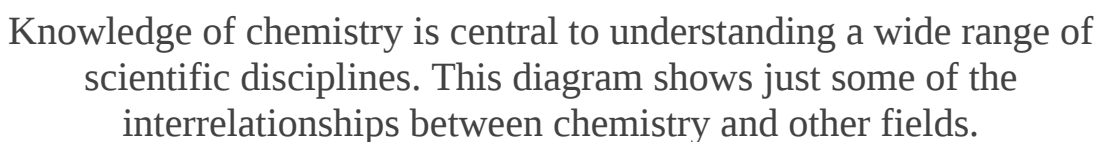


This portrayal shows an alchemist's workshop circa 1580. Although alchemy made some useful contributions to how to manipulate matter, it was not scientific by modern standards. (credit: Chemical Heritage Foundation)

From alchemy came the historical progressions that led to modern chemistry: the isolation of drugs from natural sources, metallurgy, and the dye industry. Today, chemistry continues to deepen our understanding and improve our ability to harness and control the behavior of matter. This effort has been so successful that many people do not realize either the central position of chemistry among the sciences or the importance and universality of chemistry in daily life.

Chemistry: The Central Science

Chemistry is sometimes referred to as “the central science” due to its interconnectedness with a vast array of other STEM disciplines (STEM stands for areas of study in the science, technology, engineering, and math fields). Chemistry and the language of chemists play vital roles in biology, medicine, materials science, forensics, environmental science, and many other fields ([\[link\]](#)). The basic principles of physics are essential for understanding many aspects of chemistry, and there is extensive overlap between many subdisciplines within the two fields, such as chemical physics and nuclear chemistry. Mathematics, computer science, and information theory provide important tools that help us calculate, interpret, describe, and generally make sense of the chemical world. Biology and chemistry converge in biochemistry, which is crucial to understanding the many complex factors and processes that keep living organisms (such as us) alive. Chemical engineering, materials science, and nanotechnology combine chemical principles and empirical findings to produce useful substances, ranging from gasoline to fabrics to electronics. Agriculture, food science, veterinary science, and brewing and wine making help provide sustenance in the form of food and drink to the world’s population. Medicine, pharmacology, biotechnology, and botany identify and produce substances that help keep us healthy. Environmental science, geology, oceanography, and atmospheric science incorporate many chemical ideas to help us better understand and protect our physical world. Chemical ideas are used to help understand the universe in astronomy and cosmology.

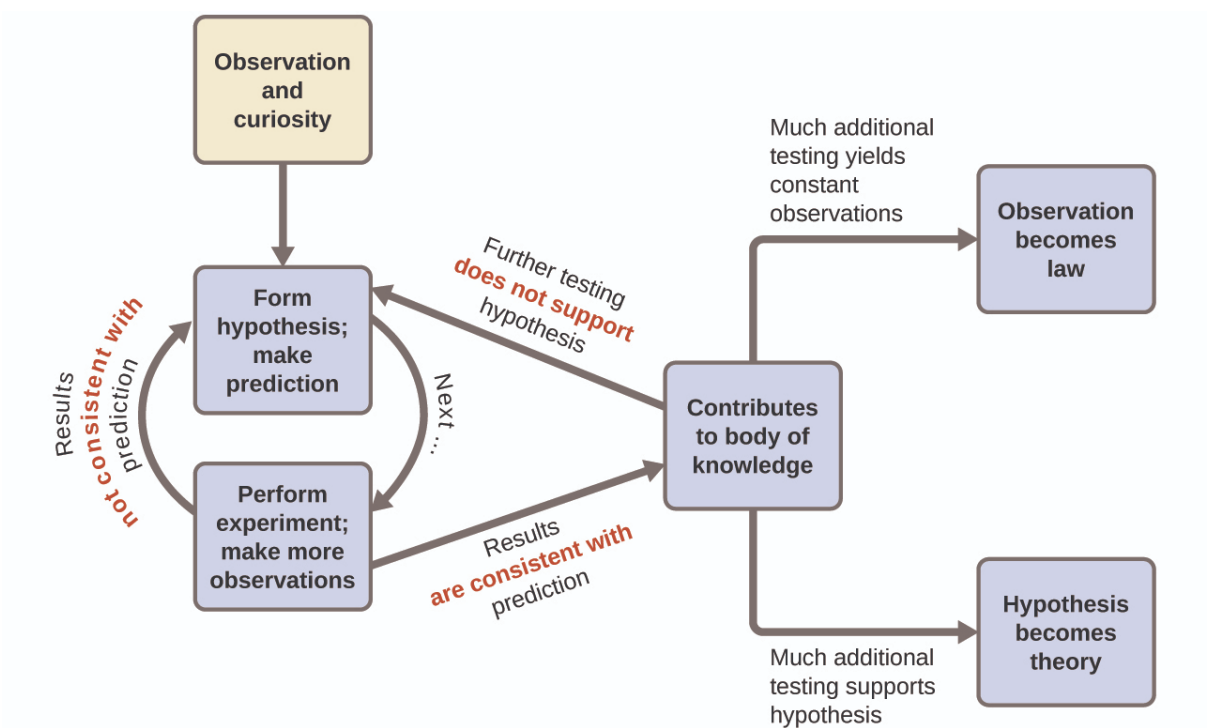


The Scientific Method

Chemistry is a science based on observation and experimentation. Doing chemistry involves attempting to answer questions and explain observations in terms of the laws and theories of chemistry, using procedures that are

accepted by the scientific community. There is no single route to answering a question or explaining an observation, but there is an aspect common to every approach: Each uses knowledge based on experiments that can be reproduced to verify the results. Some routes involve a **hypothesis**, a tentative explanation of observations that acts as a guide for gathering and checking information. We test a hypothesis by experimentation, calculation, and/or comparison with the experiments of others and then refine it as needed.

Some hypotheses are attempts to explain the behavior that is summarized in laws. The **laws** of science summarize a vast number of experimental observations, and describe or predict some facet of the natural world. If such a hypothesis turns out to be capable of explaining a large body of experimental data, it can reach the status of a theory. Scientific **theories** are well-substantiated, comprehensive, testable explanations of particular aspects of nature. Theories are accepted because they provide satisfactory explanations, but they can be modified if new data become available. The path of discovery that leads from question and observation to law or hypothesis to theory, combined with experimental verification of the hypothesis and any necessary modification of the theory, is called the **scientific method** ([\[link\]](#)).



The scientific method follows a process similar to the one shown in this diagram. All the key components are shown, in roughly the right order. Scientific progress is seldom neat and clean: It requires open inquiry and the reworking of questions and ideas in response to findings.

The Domains of Chemistry

Chemists study and describe the behavior of matter and energy in three different domains: macroscopic, microscopic, and symbolic. These domains provide different ways of considering and describing chemical behavior.

Macro is a Greek word that means “large.” The **macroscopic domain** is familiar to us: It is the realm of everyday things that are large enough to be sensed directly by human sight or touch. In daily life, this includes the food you eat and the breeze you feel on your face. The macroscopic domain includes everyday and laboratory chemistry, where we observe and measure

physical and chemical properties, or changes such as density, solubility, and flammability.

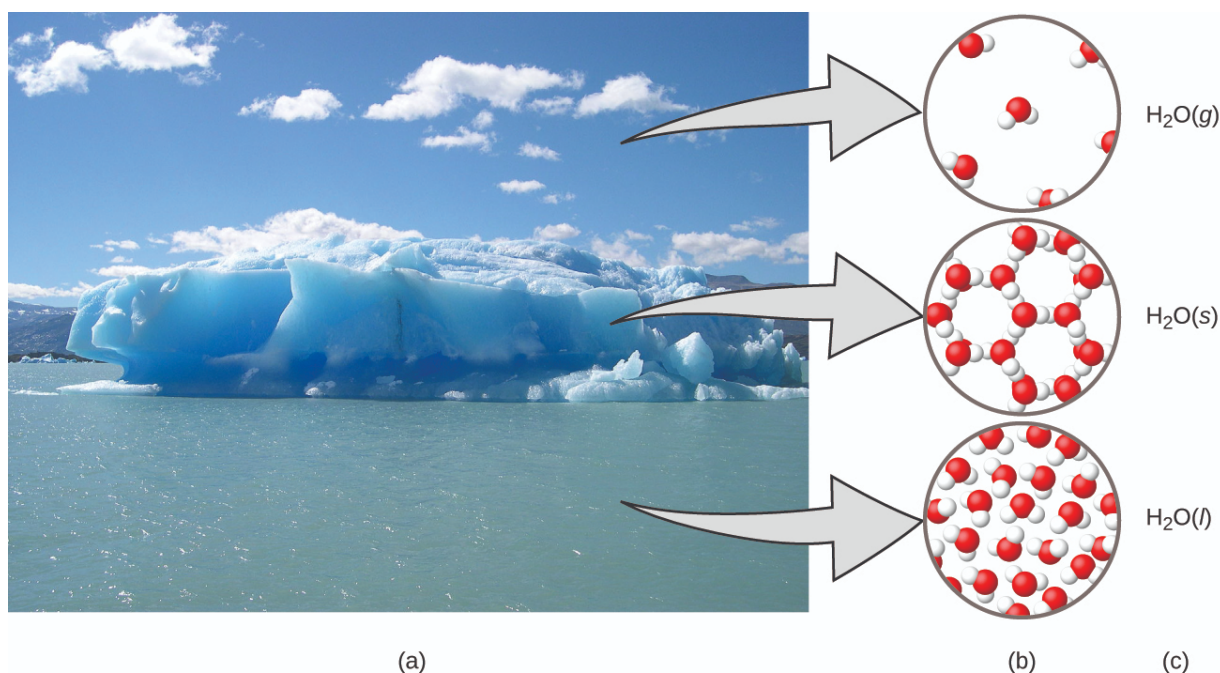
The **microscopic domain** of chemistry is almost always visited in the imagination. *Micro* also comes from Greek and means “small.” Some aspects of the microscopic domains are visible through a microscope, such as a magnified image of graphite or bacteria. Viruses, for instance, are too small to be seen with the naked eye, but when we’re suffering from a cold, we’re reminded of how real they are.

However, most of the subjects in the microscopic domain of chemistry—such as atoms and molecules—are too small to be seen even with standard microscopes and often must be pictured in the mind. Other components of the microscopic domain include ions and electrons, protons and neutrons, and chemical bonds, each of which is far too small to see. This domain includes the individual metal atoms in a wire, the ions that compose a salt crystal, the changes in individual molecules that result in a color change, the conversion of nutrient molecules into tissue and energy, and the evolution of heat as bonds that hold atoms together are created.

The **symbolic domain** contains the specialized language used to represent components of the macroscopic and microscopic domains. Chemical symbols (such as those used in the periodic table), chemical formulas, and chemical equations are part of the symbolic domain, as are graphs and drawings. We can also consider calculations as part of the symbolic domain. These symbols play an important role in chemistry because they help interpret the behavior of the macroscopic domain in terms of the components of the microscopic domain. One of the challenges for students learning chemistry is recognizing that the same symbols can represent different things in the macroscopic and microscopic domains, and one of the features that makes chemistry fascinating is the use of a domain that must be imagined to explain behavior in a domain that can be observed.

A helpful way to understand the three domains is via the essential and ubiquitous substance of water. That water is a liquid at moderate temperatures, will freeze to form a solid at lower temperatures, and boil to form a gas at higher temperatures ([\[link\]](#)) are macroscopic observations. But some properties of water fall into the microscopic domain—what we

cannot observe with the naked eye. The description of water as comprised of two hydrogen atoms and one oxygen atom, and the explanation of freezing and boiling in terms of attractions between these molecules, is within the microscopic arena. The formula H_2O , which can describe water at either the macroscopic or microscopic levels, is an example of the symbolic domain. The abbreviations (*g*) for gas, (*s*) for solid, and (*l*) for liquid are also symbolic.



(a) Moisture in the air, icebergs, and the ocean represent water in the macroscopic domain. (b) At the molecular level (microscopic domain), gas molecules are far apart and disorganized, solid water molecules are close together and organized, and liquid molecules are close together and disorganized. (c) The formula H_2O symbolizes water, and (*g*), (*s*), and (*l*) symbolize its phases. Note that clouds are actually comprised of either very small liquid water droplets or solid water crystals; gaseous water in our atmosphere is not visible to the naked eye, although it may be sensed as humidity. (credit a: modification of work by “Gorkaazk”/Wikimedia Commons)

Key Concepts and Summary

Chemistry deals with the composition, structure, and properties of matter, and the ways by which various forms of matter may be interconverted. Thus, it occupies a central place in the study and practice of science and technology. Chemists use the scientific method to perform experiments, pose hypotheses, and formulate laws and develop theories, so that they can better understand the behavior of the natural world. To do so, they operate in the macroscopic, microscopic, and symbolic domains. Chemists measure, analyze, purify, and synthesize a wide variety of substances that are important to our lives.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Explain how you could experimentally determine whether the outside temperature is higher or lower than 0°C (32°F) without using a thermometer.

Solution:

Place a glass of water outside. It will freeze if the temperature is below 0°C .

Exercise:

Problem:

Identify each of the following statements as being most similar to a hypothesis, a law, or a theory. Explain your reasoning.

- (a) Falling barometric pressure precedes the onset of bad weather.
- (b) All life on earth has evolved from a common, primitive organism through the process of natural selection.

(c) My truck's gas mileage has dropped significantly, probably because it's due for a tune-up.

Exercise:

Problem:

Identify each of the following statements as being most similar to a hypothesis, a law, or a theory. Explain your reasoning.

- (a) The pressure of a sample of gas is directly proportional to the temperature of the gas.
 - (b) Matter consists of tiny particles that can combine in specific ratios to form substances with specific properties.
 - (c) At a higher temperature, solids (such as salt or sugar) will dissolve better in water.
-

Solution:

(a) law (states a consistently observed phenomenon, can be used for prediction); (b) theory (a widely accepted explanation of the behavior of matter); (c) hypothesis (a tentative explanation, can be investigated by experimentation)

Exercise:

Problem:

Identify each of the underlined items as a part of either the macroscopic domain, the microscopic domain, or the symbolic domain of chemistry. For any in the symbolic domain, indicate whether they are symbols for a macroscopic or a microscopic feature.

- (a) The mass of a lead pipe is 14 lb.
- (b) The mass of a certain chlorine atom is 35 amu.
- (c) A bottle with a label that reads Al contains aluminum metal.

(d) Al is the symbol for an aluminum atom.

Exercise:

Problem:

Identify each of the underlined items as a part of either the macroscopic domain, the microscopic domain, or the symbolic domain of chemistry. For those in the symbolic domain, indicate whether they are symbols for a macroscopic or a microscopic feature.

(a) A certain molecule contains one H atom and one Cl atom.

(b) Copper wire has a density of about 8 g/cm^3 .

(c) The bottle contains 15 grams of Ni powder.

(d) A sulfur molecule is composed of eight sulfur atoms.

Solution:

(a) symbolic, microscopic; (b) macroscopic; (c) symbolic, macroscopic; (d) microscopic

Exercise:

Problem:

According to one theory, the pressure of a gas increases as its volume decreases because the molecules in the gas have to move a shorter distance to hit the walls of the container. Does this theory follow a macroscopic or microscopic description of chemical behavior? Explain your answer.

Exercise:

Problem:

The amount of heat required to melt 2 lbs of ice is twice the amount of heat required to melt 1 lb of ice. Is this observation a macroscopic or microscopic description of chemical behavior? Explain your answer.

Solution:

Macroscopic. The heat required is determined from macroscopic properties.

Glossary

chemistry

study of the composition, properties, and interactions of matter

hypothesis

tentative explanation of observations that acts as a guide for gathering and checking information

law

statement that summarizes a vast number of experimental observations, and describes or predicts some aspect of the natural world

macroscopic domain

realm of everyday things that are large enough to sense directly by human sight and touch

microscopic domain

realm of things that are much too small to be sensed directly

scientific method

path of discovery that leads from question and observation to law or hypothesis to theory, combined with experimental verification of the hypothesis and any necessary modification of the theory

symbolic domain

specialized language used to represent components of the macroscopic and microscopic domains, such as chemical symbols, chemical formulas, chemical equations, graphs, drawings, and calculations

theory

well-substantiated, comprehensive, testable explanation of a particular aspect of nature

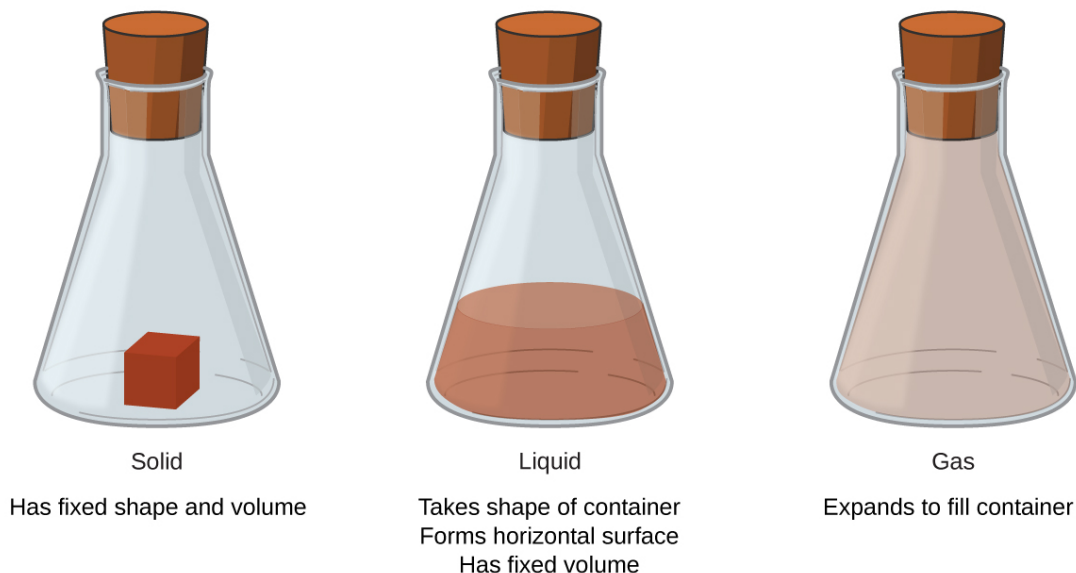
Phases and Classification of Matter

By the end of this section, you will be able to:

- Describe the basic properties of each physical state of matter: solid, liquid, and gas
- Define and give examples of atoms and molecules
- Classify matter as an element, compound, homogeneous mixture, or heterogeneous mixture with regard to its physical state and composition
- Distinguish between mass and weight
- Apply the law of conservation of matter

Matter is defined as anything that occupies space and has mass, and it is all around us. Solids and liquids are more obviously matter: We can see that they take up space, and their weight tells us that they have mass. Gases are also matter; if gases did not take up space, a balloon would stay collapsed rather than inflate when filled with gas.

Solids, liquids, and gases are the three states of matter commonly found on earth ([link](#)). A **solid** is rigid and possesses a definite shape. A **liquid** flows and takes the shape of a container, except that it forms a flat or slightly curved upper surface when acted upon by gravity. (In zero gravity, liquids assume a spherical shape.) Both liquid and solid samples have volumes that are very nearly independent of pressure. A **gas** takes both the shape and volume of its container.



The three most common states or phases of matter are solid, liquid, and gas.

A fourth state of matter, plasma, occurs naturally in the interiors of stars. A **plasma** is a gaseous state of matter that contains appreciable numbers of electrically charged particles ([link](#)). The presence of these charged particles imparts unique properties to plasmas that justify their classification as a state of matter distinct from gases. In addition to stars,

plasmas are found in some other high-temperature environments (both natural and man-made), such as lightning strikes, certain television screens, and specialized analytical instruments used to detect trace amounts of metals.



A plasma torch can be used to cut metal. (credit: “Hypertherm”/Wikimedia Commons)

Note:



In a tiny cell in a plasma television, the plasma emits ultraviolet light, which in turn causes the display at that location to appear a specific color. The composite of these tiny dots of

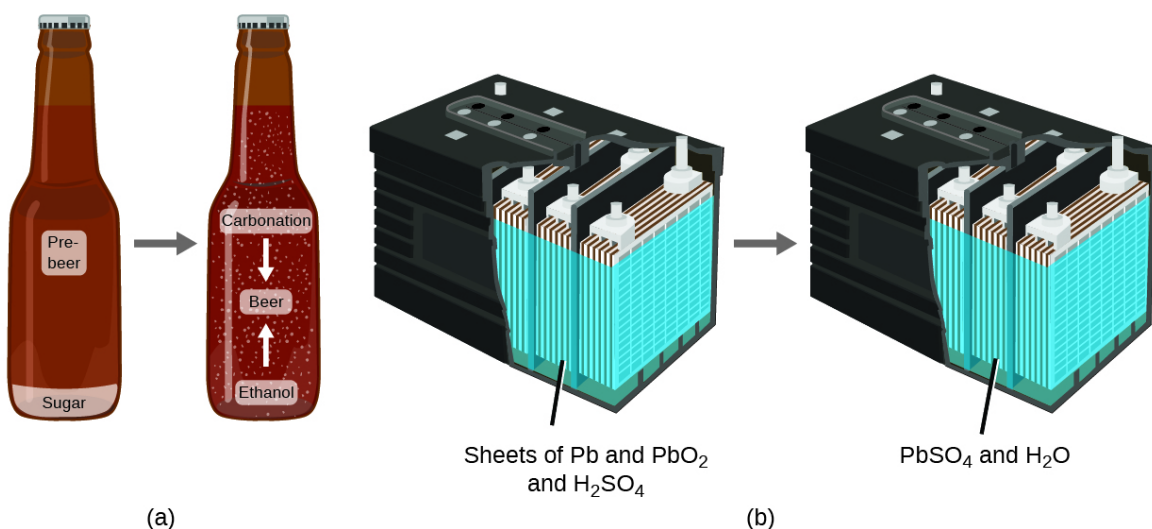
color makes up the image that you see. Watch this [video](#) to learn more about plasma and the places you encounter it.

Some samples of matter appear to have properties of solids, liquids, and/or gases at the same time. This can occur when the sample is composed of many small pieces. For example, we can pour sand as if it were a liquid because it is composed of many small grains of solid sand. Matter can also have properties of more than one state when it is a mixture, such as with clouds. Clouds appear to behave somewhat like gases, but they are actually mixtures of air (gas) and tiny particles of water (liquid or solid).

The **mass** of an object is a measure of the amount of matter in it. One way to measure an object's mass is to measure the force it takes to accelerate the object. It takes much more force to accelerate a car than a bicycle because the car has much more mass. A more common way to determine the mass of an object is to use a balance to compare its mass with a standard mass.

Although weight is related to mass, it is not the same thing. **Weight** refers to the force that gravity exerts on an object. This force is directly proportional to the mass of the object. The weight of an object changes as the force of gravity changes, but its mass does not. An astronaut's mass does not change just because she goes to the moon. But her weight on the moon is only one-sixth her earth-bound weight because the moon's gravity is only one-sixth that of the earth's. She may feel "weightless" during her trip when she experiences negligible external forces (gravitational or any other), although she is, of course, never "massless."

The **law of conservation of matter** summarizes many scientific observations about matter: It states that *there is no detectable change in the total quantity of matter present when matter converts from one type to another (a chemical change) or changes among solid, liquid, or gaseous states (a physical change)*. Brewing beer and the operation of batteries provide examples of the conservation of matter ([link](#)). During the brewing of beer, the ingredients (water, yeast, grains, malt, hops, and sugar) are converted into beer (water, alcohol, carbonation, and flavoring substances) with no actual loss of substance. This is most clearly seen during the bottling process, when glucose turns into ethanol and carbon dioxide, and the total mass of the substances does not change. This can also be seen in a lead-acid car battery: The original substances (lead, lead oxide, and sulfuric acid), which are capable of producing electricity, are changed into other substances (lead sulfate and water) that do not produce electricity, with no change in the actual amount of matter.

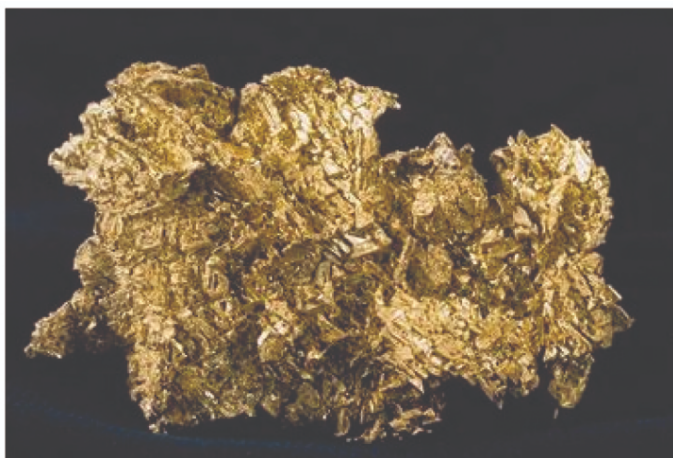


(a) The mass of beer precursor materials is the same as the mass of beer produced: Sugar has become alcohol and carbonation. (b) The mass of the lead, lead oxide plates, and sulfuric acid that goes into the production of electricity is exactly equal to the mass of lead sulfate and water that is formed.

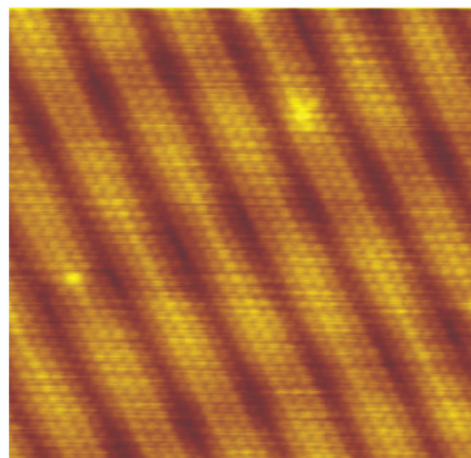
Although this conservation law holds true for all conversions of matter, convincing examples are few and far between because, outside of the controlled conditions in a laboratory, we seldom collect all of the material that is produced during a particular conversion. For example, when you eat, digest, and assimilate food, all of the matter in the original food is preserved. But because some of the matter is incorporated into your body, and much is excreted as various types of waste, it is challenging to verify by measurement.

Atoms and Molecules

An **atom** is the smallest particle of an element that has the properties of that element and can enter into a chemical combination. Consider the element gold, for example. Imagine cutting a gold nugget in half, then cutting one of the halves in half, and repeating this process until a piece of gold remained that was so small that it could not be cut in half (regardless of how tiny your knife may be). This minimally sized piece of gold is an atom (from the Greek *atomos*, meaning “indivisible”) ([link](#)). This atom would no longer be gold if it were divided any further.



(a)

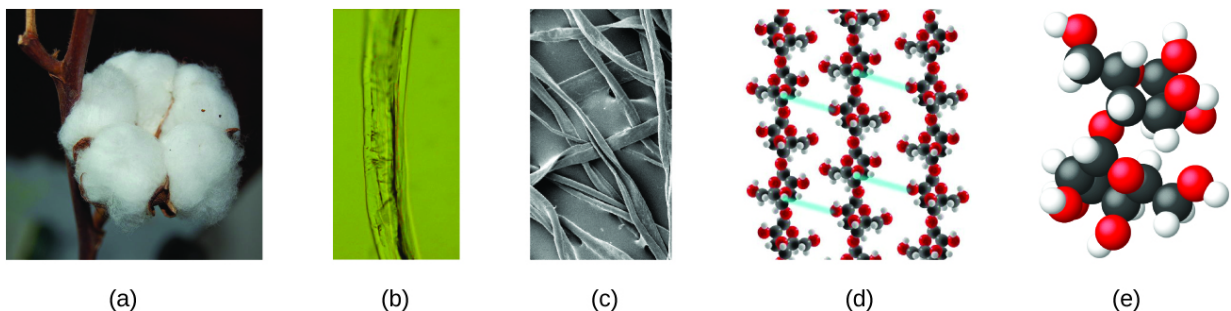


(b)

(a) This photograph shows a gold nugget. (b) A scanning-tunneling microscope (STM) can generate views of the surfaces of solids, such as this image of a gold crystal. Each sphere represents one gold atom. (credit a: modification of work by United States Geological Survey; credit b: modification of work by “Erwinrossen”/Wikimedia Commons)

The first suggestion that matter is composed of atoms is attributed to the Greek philosophers Leucippus and Democritus, who developed their ideas in the 5th century BCE. However, it was not until the early nineteenth century that John Dalton (1766–1844), a British schoolteacher with a keen interest in science, supported this hypothesis with quantitative measurements. Since that time, repeated experiments have confirmed many aspects of this hypothesis, and it has become one of the central theories of chemistry. Other aspects of Dalton’s atomic theory are still used but with minor revisions (details of Dalton’s theory are provided in the chapter on atoms and molecules).

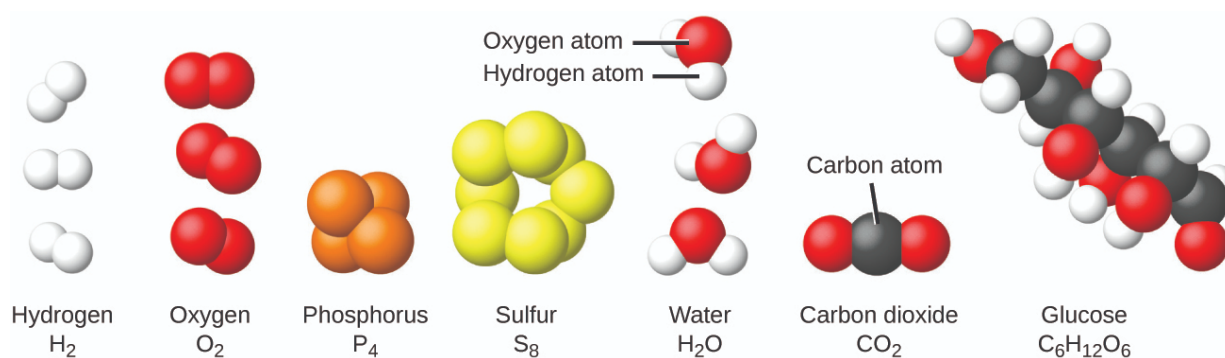
An atom is so small that its size is difficult to imagine. One of the smallest things we can see with our unaided eye is a single thread of a spider web: These strands are about $1/10,000$ of a centimeter (0.0001 cm) in diameter. Although the cross-section of one strand is almost impossible to see without a microscope, it is huge on an atomic scale. A single carbon atom in the web has a diameter of about 0.000000015 centimeter, and it would take about 7000 carbon atoms to span the diameter of the strand. To put this in perspective, if a carbon atom were the size of a dime, the cross-section of one strand would be larger than a football field, which would require about 150 million carbon atom “dimes” to cover it. ([link](#)) shows increasingly close microscopic and atomic-level views of ordinary cotton.



These images provide an increasingly closer view: (a) a cotton boll, (b) a single cotton fiber viewed under an optical microscope (magnified 40 times), (c) an image of a cotton fiber obtained with an electron microscope (much higher magnification than with the optical microscope); and (d and e) atomic-level models of the fiber (spheres of different colors represent atoms of different elements). (credit c: modification of work by “Featheredtar”/Wikimedia Commons)

An atom is so light that its mass is also difficult to imagine. A billion lead atoms (1,000,000,000 atoms) weigh about 3×10^{-13} grams, a mass that is far too light to be weighed on even the world’s most sensitive balances. It would require over 300,000,000,000,000 lead atoms (300 trillion, or 3×10^{14}) to be weighed, and they would weigh only 0.0000001 gram.

It is rare to find collections of individual atoms. Only a few elements, such as the gases helium, neon, and argon, consist of a collection of individual atoms that move about independently of one another. Other elements, such as the gases hydrogen, nitrogen, oxygen, and chlorine, are composed of units that consist of pairs of atoms ([link](#)). One form of the element phosphorus consists of units composed of four phosphorus atoms. The element sulfur exists in various forms, one of which consists of units composed of eight sulfur atoms. These units are called molecules. A **molecule** consists of two or more atoms joined by strong forces called chemical bonds. The atoms in a molecule move around as a unit, much like the cans of soda in a six-pack or a bunch of keys joined together on a single key ring. A molecule may consist of two or more identical atoms, as in the molecules found in the elements hydrogen, oxygen, and sulfur, or it may consist of two or more different atoms, as in the molecules found in water. Each water molecule is a unit that contains two hydrogen atoms and one oxygen atom. Each glucose molecule is a unit that contains 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. Like atoms, molecules are incredibly small and light. If an ordinary glass of water were enlarged to the size of the earth, the water molecules inside it would be about the size of golf balls.



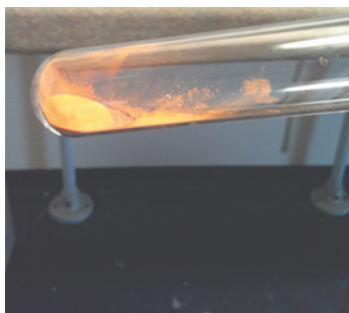
The elements hydrogen, oxygen, phosphorus, and sulfur form molecules consisting of two or more atoms of the same element. The compounds water, carbon dioxide, and glucose consist of combinations of atoms of different elements.

Classifying Matter

We can classify matter into several categories. Two broad categories are mixtures and pure substances. A **pure substance** has a constant composition. All specimens of a pure substance have exactly the same makeup and properties. Any sample of sucrose (table sugar) consists of 42.1% carbon, 6.5% hydrogen, and 51.4% oxygen by mass. Any sample of sucrose also has the same physical properties, such as melting point, color, and sweetness, regardless of the source from which it is isolated.

We can divide pure substances into two classes: elements and compounds. Pure substances that cannot be broken down into simpler substances by chemical changes are called **elements**. Iron, silver, gold, aluminum, sulfur, oxygen, and copper are familiar examples of the more than 100 known elements, of which about 90 occur naturally on the earth, and two dozen or so have been created in laboratories.

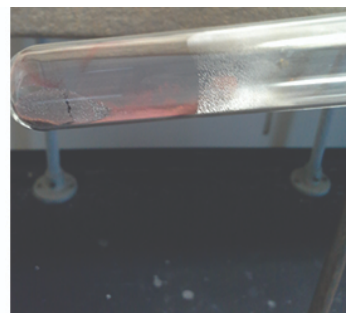
Pure substances that can be broken down by chemical changes are called **compounds**. This breakdown may produce either elements or other compounds, or both. Mercury(II) oxide, an orange, crystalline solid, can be broken down by heat into the elements mercury and oxygen ([link](#)). When heated in the absence of air, the compound sucrose is broken down into the element carbon and the compound water. (The initial stage of this process, when the sugar is turning brown, is known as caramelization—this is what imparts the characteristic sweet and nutty flavor to caramel apples, caramelized onions, and caramel). Silver(I) chloride is a white solid that can be broken down into its elements, silver and chlorine, by absorption of light. This property is the basis for the use of this compound in photographic films and photochromic eyeglasses (those with lenses that darken when exposed to light).



(a)



(b)



(c)

(a)The compound mercury(II) oxide, (b)when heated, (c) decomposes into silvery droplets of liquid mercury and invisible oxygen gas. (credit: modification of work by Paul Flowers)

Note:



Many compounds break down when heated. This [site](#) shows the breakdown of mercury oxide, HgO . You can also view an example of the [photochemical decomposition of silver chloride](#) (AgCl), the basis of early photography.

The properties of combined elements are different from those in the free, or uncombined, state. For example, white crystalline sugar (sucrose) is a compound resulting from the chemical combination of the element carbon, which is a black solid in one of its uncombined forms, and the two elements hydrogen and oxygen, which are colorless gases when uncombined. Free sodium, an element that is a soft, shiny, metallic solid, and free chlorine, an element that is a yellow-green gas, combine to form sodium chloride (table salt), a compound that is a white, crystalline solid.

A **mixture** is composed of two or more types of matter that can be present in varying amounts and can be separated by physical changes, such as evaporation (you will learn more about this later). A mixture with a composition that varies from point to point is called a **heterogeneous mixture**. Italian dressing is an example of a heterogeneous mixture ([link](#)).

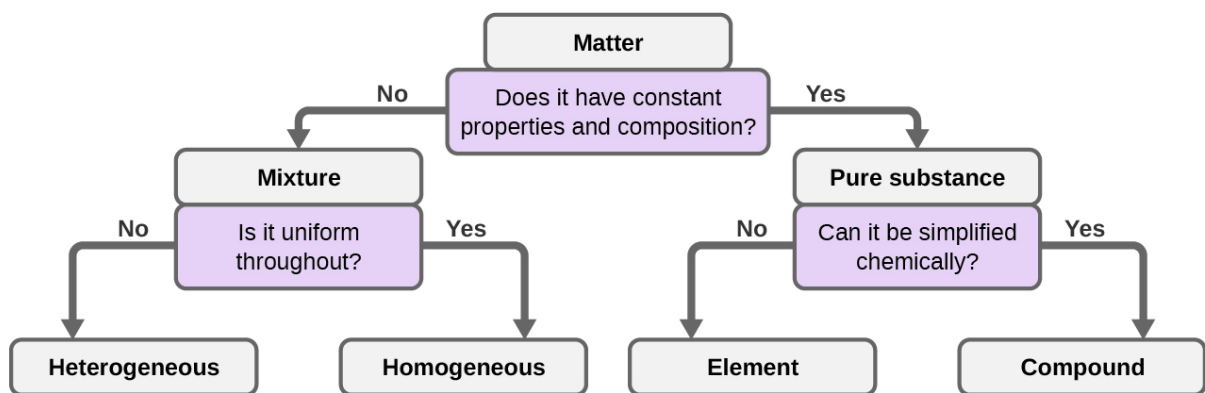
Its composition can vary because we can make it from varying amounts of oil, vinegar, and herbs. It is not the same from point to point throughout the mixture—one drop may be mostly vinegar, whereas a different drop may be mostly oil or herbs because the oil and vinegar separate and the herbs settle. Other examples of heterogeneous mixtures are chocolate chip cookies (we can see the separate bits of chocolate, nuts, and cookie dough) and granite (we can see the quartz, mica, feldspar, and more).

A **homogeneous mixture**, also called a **solution**, exhibits a uniform composition and appears visually the same throughout. An example of a solution is a sports drink, consisting of water, sugar, coloring, flavoring, and electrolytes mixed together uniformly ([link](#)). Each drop of a sports drink tastes the same because each drop contains the same amounts of water, sugar, and other components. Note that the composition of a sports drink can vary—it could be made with somewhat more or less sugar, flavoring, or other components, and still be a sports drink. Other examples of homogeneous mixtures include air, maple syrup, gasoline, and a solution of salt in water.



(a) Oil and vinegar salad dressing is a heterogeneous mixture because its composition is not uniform throughout. (b) A commercial sports drink is a homogeneous mixture because its composition is uniform throughout. (credit a “left”: modification of work by John Mayer; credit a “right”: modification of work by Umberto Salvagnin; credit b “left: modification of work by Jeff Bedford)

Although there are just over 100 elements, tens of millions of chemical compounds result from different combinations of these elements. Each compound has a specific composition and possesses definite chemical and physical properties by which we can distinguish it from all other compounds. And, of course, there are innumerable ways to combine elements and compounds to form different mixtures. A summary of how to distinguish between the various major classifications of matter is shown in ([link](#)).



Depending on its properties, a given substance can be classified as a homogeneous mixture, a heterogeneous mixture, a compound, or an element.

Eleven elements make up about 99% of the earth's crust and atmosphere ([link](#)). Oxygen constitutes nearly one-half and silicon about one-quarter of the total quantity of these elements. A majority of elements on earth are found in chemical combinations with other elements; about one-quarter of the elements are also found in the free state.

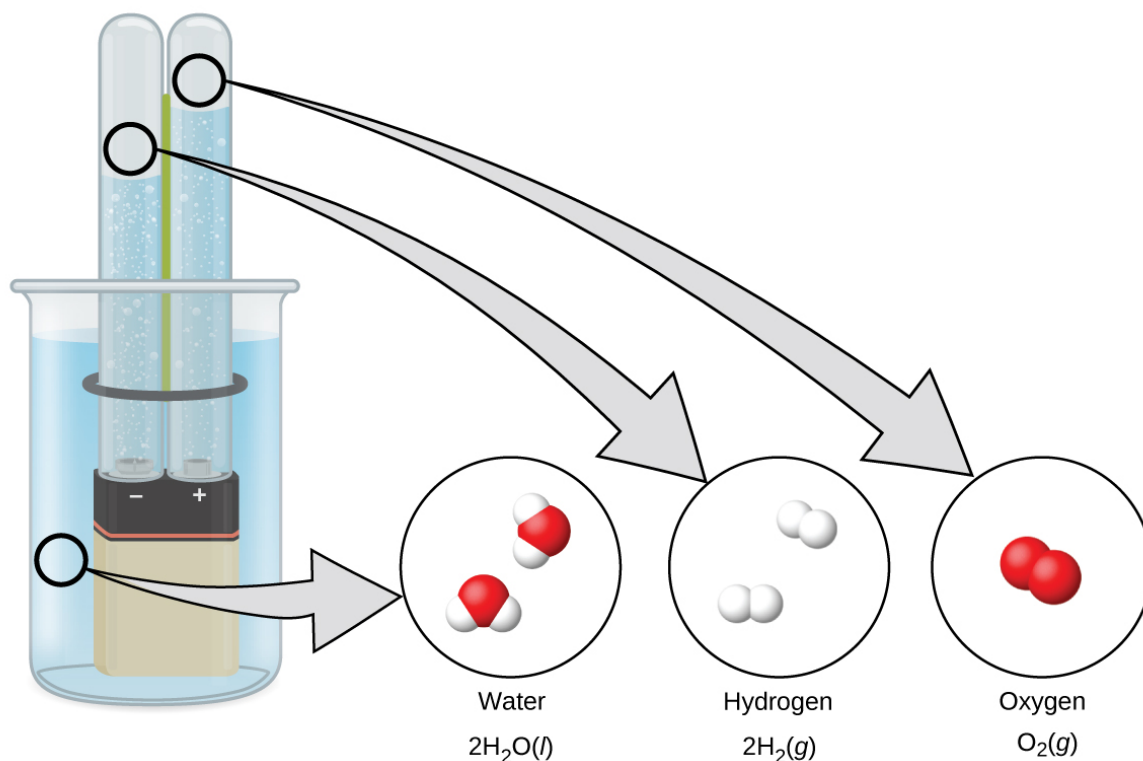
Elemental Composition of Earth						
Element	Symbol	Percent Mass		Element	Symbol	Percent Mass
oxygen	O	49.20		chlorine	Cl	0.19
silicon	Si	25.67		phosphorus	P	0.11
aluminum	Al	7.50		manganese	Mn	0.09
iron	Fe	4.71		carbon	C	0.08
calcium	Ca	3.39		sulfur	S	0.06
sodium	Na	2.63		barium	Ba	0.04
potassium	K	2.40		nitrogen	N	0.03

Elemental Composition of Earth						
Element	Symbol	Percent Mass		Element	Symbol	Percent Mass
magnesium	Mg	1.93		fluorine	F	0.03
hydrogen	H	0.87		strontium	Sr	0.02
titanium	Ti	0.58		all others	-	0.47

Note:

Decomposition of Water / Production of Hydrogen

Water consists of the elements hydrogen and oxygen combined in a 2 to 1 ratio. Water can be broken down into hydrogen and oxygen gases by the addition of energy. One way to do this is with a battery or power supply, as shown in ([link](#)).

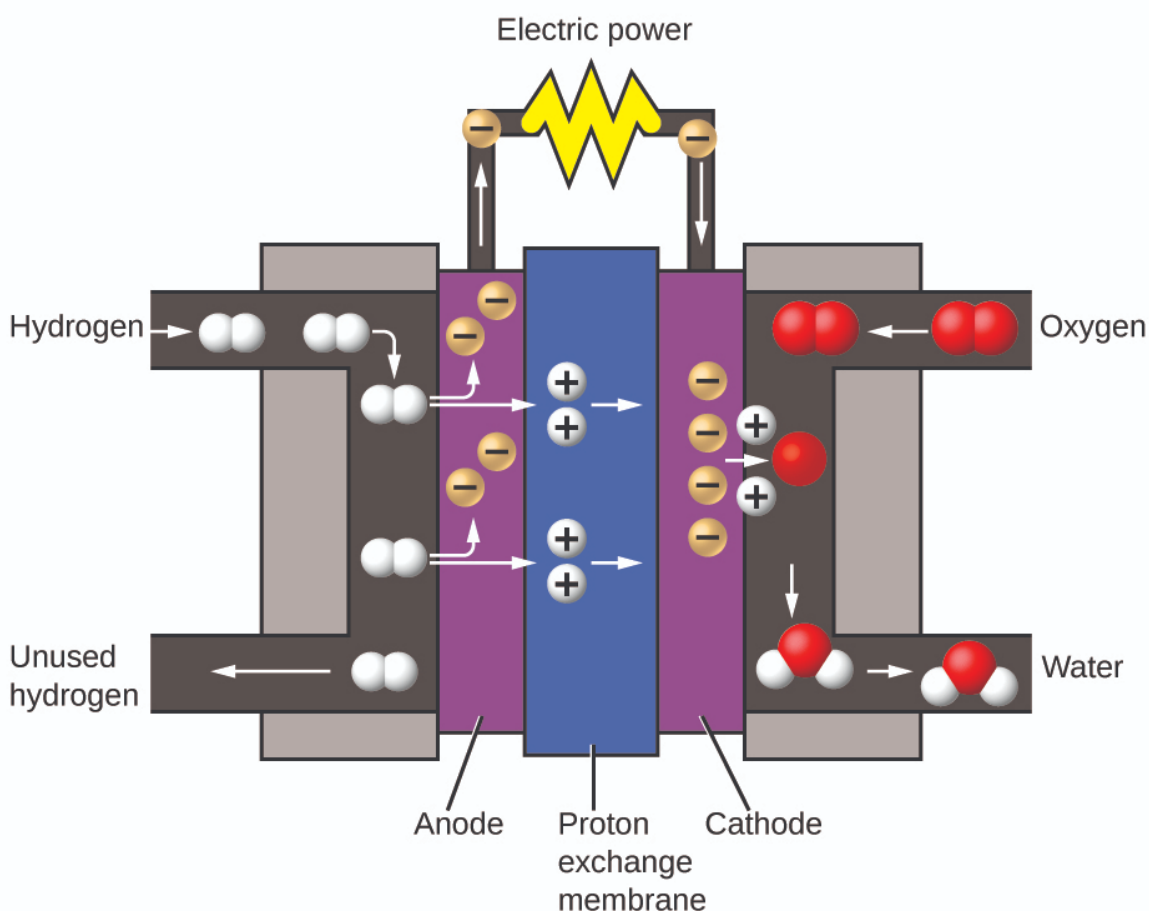


The decomposition of water is shown at the macroscopic, microscopic, and symbolic levels. The battery provides an electric current (microscopic) that decomposes water. At the macroscopic level, the liquid separates into the gases hydrogen (on the left) and

oxygen (on the right). Symbolically, this change is presented by showing how liquid H_2O separates into H_2 and O_2 gases.

The breakdown of water involves a rearrangement of the atoms in water molecules into different molecules, each composed of two hydrogen atoms and two oxygen atoms, respectively. Two water molecules form one oxygen molecule and two hydrogen molecules. The representation for what occurs, $2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g)$, will be explored in more depth in later chapters.

The two gases produced have distinctly different properties. Oxygen is not flammable but is required for combustion of a fuel, and hydrogen is highly flammable and a potent energy source. How might this knowledge be applied in our world? One application involves research into more fuel-efficient transportation. Fuel-cell vehicles (FCV) run on hydrogen instead of gasoline ([link](#)). They are more efficient than vehicles with internal combustion engines, are nonpolluting, and reduce greenhouse gas emissions, making us less dependent on fossil fuels. FCVs are not yet economically viable, however, and current hydrogen production depends on natural gas. If we can develop a process to economically decompose water, or produce hydrogen in another environmentally sound way, FCVs may be the way of the future.

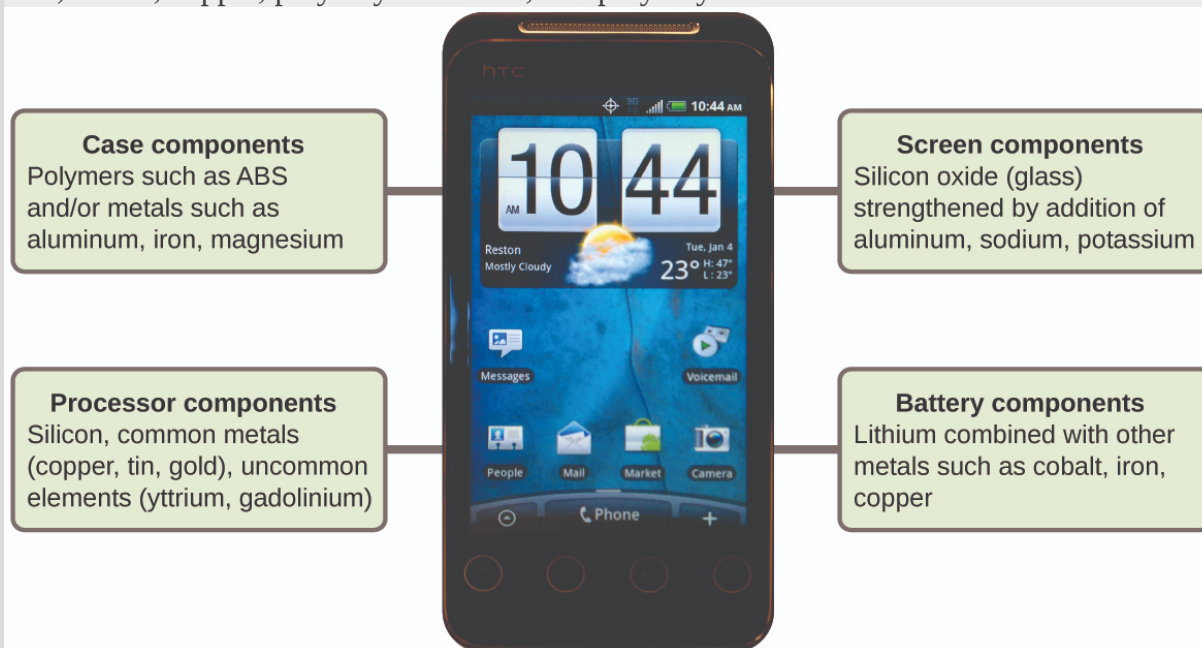


A fuel cell generates electrical energy from hydrogen and oxygen via an electrochemical process and produces only water as the waste product.

Note:

Chemistry of Cell Phones

Imagine how different your life would be without cell phones ([link](#)) and other smart devices. Cell phones are made from numerous chemical substances, which are extracted, refined, purified, and assembled using an extensive and in-depth understanding of chemical principles. About 30% of the elements that are found in nature are found within a typical smart phone. The case/body/frame consists of a combination of sturdy, durable polymers comprised primarily of carbon, hydrogen, oxygen, and nitrogen [acrylonitrile butadiene styrene (ABS) and polycarbonate thermoplastics], and light, strong, structural metals, such as aluminum, magnesium, and iron. The display screen is made from a specially toughened glass (silica glass strengthened by the addition of aluminum, sodium, and potassium) and coated with a material to make it conductive (such as indium tin oxide). The circuit board uses a semiconductor material (usually silicon); commonly used metals like copper, tin, silver, and gold; and more unfamiliar elements such as yttrium, praseodymium, and gadolinium. The battery relies upon lithium ions and a variety of other materials, including iron, cobalt, copper, polyethylene oxide, and polyacrylonitrile.



Almost one-third of naturally occurring elements are used to make a cell phone.
(credit: modification of work by John Taylor)

Key Concepts and Summary

Matter is anything that occupies space and has mass. The basic building block of matter is the atom, the smallest unit of an element that can enter into combinations with atoms of the same or other elements. In many substances, atoms are combined into molecules. On earth, matter commonly exists in three states: solids, of fixed shape and volume; liquids, of variable shape but fixed volume; and gases, of variable shape and volume. Under high-temperature conditions, matter also can exist as a plasma. Most matter is a mixture: It is composed of two or more types of matter that can be present in varying amounts and can be separated by physical means. Heterogeneous mixtures vary in composition from point to point; homogeneous mixtures have the same composition from point to point. Pure substances consist of only one type of matter. A pure substance can be an element, which consists of only one type of atom and cannot be broken down by a chemical change, or a compound, which consists of two or more types of atoms.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Why do we use an object's mass, rather than its weight, to indicate the amount of matter it contains?

Exercise:

Problem:

What properties distinguish solids from liquids? Liquids from gases? Solids from gases?

Solution:

Liquids can change their shape (flow); solids can't. Gases can undergo large volume changes as pressure changes; liquids do not. Gases flow and change volume; solids do not.

Exercise:

Problem:

How does a heterogeneous mixture differ from a homogeneous mixture? How are they similar?

Exercise:

Problem:

How does a homogeneous mixture differ from a pure substance? How are they similar?

Solution:

The mixture can have a variety of compositions; a pure substance has a definite composition. Both have the same composition from point to point.

Exercise:

Problem: How does an element differ from a compound? How are they similar?

Exercise:**Problem:**

How do molecules of elements and molecules of compounds differ? In what ways are they similar?

Solution:

Molecules of elements contain only one type of atom; molecules of compounds contain two or more types of atoms. They are similar in that both are comprised of two or more atoms chemically bonded together.

Exercise:

Problem: How does an atom differ from a molecule? In what ways are they similar?

Exercise:**Problem:**

Many of the items you purchase are mixtures of pure compounds. Select three of these commercial products and prepare a list of the ingredients that are pure compounds.

Solution:

Answers will vary. Sample answer: Gatorade contains water, sugar, dextrose, citric acid, salt, sodium chloride, monopotassium phosphate, and sucrose acetate isobutyrate.

Exercise:

Problem: Classify each of the following as an element, a compound, or a mixture:

- (a) copper
- (b) water
- (c) nitrogen
- (d) sulfur

- (e) air
- (f) sucrose
- (g) a substance composed of molecules each of which contains two iodine atoms
- (h) gasoline

Exercise:

Problem: Classify each of the following as an element, a compound, or a mixture:

- (a) iron
- (b) oxygen
- (c) mercury oxide
- (d) pancake syrup
- (e) carbon dioxide
- (f) a substance composed of molecules each of which contains one hydrogen atom and one chlorine atom
- (g) baking soda
- (h) baking powder

Solution:

(a) element; (b) element; (c) compound; (d) mixture, (e) compound; (f) compound; (g) compound; (h) mixture

Exercise:

Problem: A sulfur atom and a sulfur molecule are not identical. What is the difference?

Exercise:

Problem:

How are the molecules in oxygen gas, the molecules in hydrogen gas, and water molecules similar? How do they differ?

Solution:

In each case, a molecule consists of two or more combined atoms. They differ in that the types of atoms change from one substance to the next.

Exercise:

Problem: We refer to astronauts in space as weightless, but not without mass. Why?

Exercise:**Problem:**

As we drive an automobile, we don't think about the chemicals consumed and produced. Prepare a list of the principal chemicals consumed and produced during the operation of an automobile.

Solution:

Gasoline (a mixture of compounds), oxygen, and to a lesser extent, nitrogen are consumed. Carbon dioxide and water are the principal products. Carbon monoxide and nitrogen oxides are produced in lesser amounts.

Exercise:**Problem:**

Matter is everywhere around us. Make a list by name of fifteen different kinds of matter that you encounter every day. Your list should include (and label at least one example of each) the following: a solid, a liquid, a gas, an element, a compound, a homogenous mixture, a heterogeneous mixture, and a pure substance.

Exercise:**Problem:**

When elemental iron corrodes it combines with oxygen in the air to ultimately form red brown iron(III) oxide which we call rust. (a) If a shiny iron nail with an initial mass of 23.2 g is weighed after being coated in a layer of rust, would you expect the mass to have increased, decreased, or remained the same? Explain. (b) If the mass of the iron nail increases to 24.1 g, what mass of oxygen combined with the iron?

Solution:

(a) Increased as it would have combined with oxygen in the air thus increasing the amount of matter and therefore the mass. (b) 0.9 g

Exercise:**Problem:**

As stated in the text, convincing examples that demonstrate the law of conservation of matter outside of the laboratory are few and far between. Indicate whether the mass would increase, decrease, or stay the same for the following scenarios where chemical reactions take place:

(a) Exactly one pound of bread dough is placed in a baking tin. The dough is cooked in an oven at 350 °F releasing a wonderful aroma of freshly baked bread during the cooking process. Is the mass of the baked loaf less than, greater than, or the same as the one pound of original dough? Explain.

(b) When magnesium burns in air a white flaky ash of magnesium oxide is produced. Is the mass of magnesium oxide less than, greater than, or the same as the original piece of magnesium? Explain.

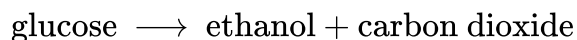
(c) Antoine Lavoisier, the French scientist credited with first stating the law of conservation of matter, heated a mixture of tin and air in a sealed flask to produce tin oxide. Did the mass of the sealed flask and contents decrease, increase, or remain the same after the heating?

Exercise:

Problem:

Yeast converts glucose to ethanol and carbon dioxide during anaerobic fermentation as depicted in the simple chemical equation here:

Equation:



(a) If 200.0 g of glucose is fully converted, what will be the total mass of ethanol and carbon dioxide produced?

(b) If the fermentation is carried out in an open container, would you expect the mass of the container and contents after fermentation to be less than, greater than, or the same as the mass of the container and contents before fermentation? Explain.

(c) If 97.7 g of carbon dioxide is produced, what mass of ethanol is produced?

Solution:

(a) 200.0 g; (b) The mass of the container and contents would decrease as carbon dioxide is a gaseous product and would leave the container. (c) 102.3 g

Glossary

atom

smallest particle of an element that can enter into a chemical combination

compound

pure substance that can be decomposed into two or more elements

element

substance that is composed of a single type of atom; a substance that cannot be decomposed by a chemical change

gas

state in which matter has neither definite volume nor shape

heterogeneous mixture

combination of substances with a composition that varies from point to point

homogeneous mixture

(also, solution) combination of substances with a composition that is uniform throughout

liquid

state of matter that has a definite volume but indefinite shape

law of conservation of matter

when matter converts from one type to another or changes form, there is no detectable change in the total amount of matter present

mass

fundamental property indicating amount of matter

matter

anything that occupies space and has mass

mixture

matter that can be separated into its components by physical means

molecule

bonded collection of two or more atoms of the same or different elements

plasma

gaseous state of matter containing a large number of electrically charged atoms and/or molecules

pure substance

homogeneous substance that has a constant composition

solid

state of matter that is rigid, has a definite shape, and has a fairly constant volume

weight

force that gravity exerts on an object

Physical and Chemical Properties

By the end of this section, you will be able to:

- Identify properties of and changes in matter as physical or chemical
- Identify properties of matter as extensive or intensive

The characteristics that enable us to distinguish one substance from another are called properties. A **physical property** is a characteristic of matter that is not associated with a change in its chemical composition. Familiar examples of physical properties include density, color, hardness, melting and boiling points, and electrical conductivity. We can observe some physical properties, such as density and color, without changing the physical state of the matter observed. Other physical properties, such as the melting temperature of iron or the freezing temperature of water, can only be observed as matter undergoes a physical change. A **physical change** is a change in the state or properties of matter without any accompanying change in its chemical composition (the identities of the substances contained in the matter). We observe a physical change when wax melts, when sugar dissolves in coffee, and when steam condenses into liquid water ([\[link\]](#)). Other examples of physical changes include magnetizing and demagnetizing metals (as is done with common antitheft security tags) and grinding solids into powders (which can sometimes yield noticeable changes in color). In each of these examples, there is a change in the physical state, form, or properties of the substance, but no change in its chemical composition.



(a)



(b)

(a) Wax undergoes a physical change when solid wax is heated and forms liquid wax. (b) Steam condensing inside a cooking pot is a physical change, as water vapor is changed into liquid water. (credit a: modification of work by “95jb14”/Wikimedia Commons; credit b: modification of work by “mjneuby”/Flickr)

The change of one type of matter into another type (or the inability to change) is a **chemical property**. Examples of chemical properties include flammability, toxicity, acidity, reactivity (many types), and heat of combustion. Iron, for example, combines with oxygen in the presence of water to form rust; chromium does not oxidize ([link](#)). Nitroglycerin is very dangerous because it explodes easily; neon poses almost no hazard because it is very unreactive.



(a)



(b)

(a) One of the chemical properties of iron is that it rusts; (b) one of the chemical properties of chromium is that it does not. (credit a: modification of work by Tony Hisgett; credit b: modification of work by “Atoma”/Wikimedia Commons)

To identify a chemical property, we look for a chemical change. A **chemical change** always produces one or more types of matter that differ from the matter present before the change. The formation of rust is a chemical

change because rust is a different kind of matter than the iron, oxygen, and water present before the rust formed. The explosion of nitroglycerin is a chemical change because the gases produced are very different kinds of matter from the original substance. Other examples of chemical changes include reactions that are performed in a lab (such as copper reacting with nitric acid), all forms of combustion (burning), and food being cooked, digested, or rotting ([link](#)).



(a)



(b)



(c)



(d)

(a) Copper and nitric acid undergo a chemical change to form copper nitrate and brown, gaseous nitrogen dioxide. (b) During the combustion of a match, cellulose in the match and oxygen from the air undergo a chemical change to form carbon dioxide and water vapor. (c) Cooking red meat causes a number of chemical changes, including the oxidation of iron in myoglobin that results in the familiar red-to-

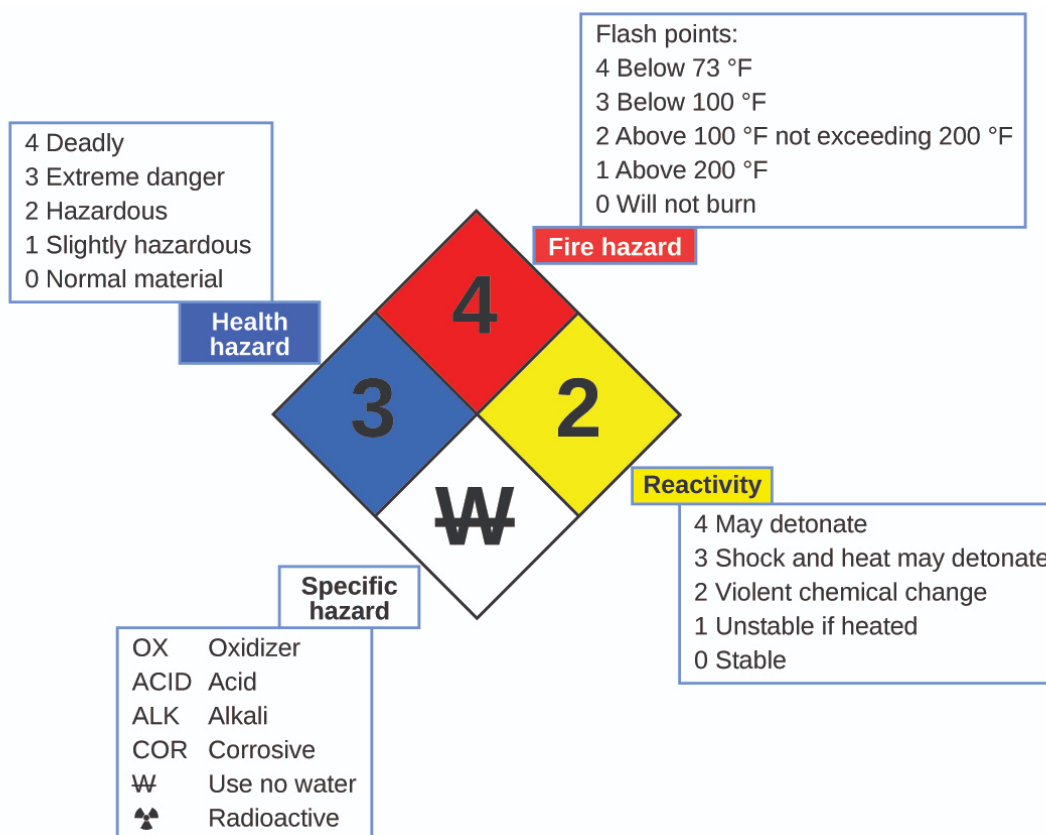
brown color change. (d) A banana turning brown is a chemical change as new, darker (and less tasty) substances form. (credit b: modification of work by Jeff Turner; credit c: modification of work by Gloria Cabada-Leman; credit d: modification of work by Roberto Verzo)

Properties of matter fall into one of two categories. If the property depends on the amount of matter present, it is an **extensive property**. The mass and volume of a substance are examples of extensive properties; for instance, a gallon of milk has a larger mass and volume than a cup of milk. The value of an extensive property is directly proportional to the amount of matter in question. If the property of a sample of matter does not depend on the amount of matter present, it is an **intensive property**. Temperature is an example of an intensive property. If the gallon and cup of milk are each at 20 °C (room temperature), when they are combined, the temperature remains at 20 °C. As another example, consider the distinct but related properties of heat and temperature. A drop of hot cooking oil splattered on your arm causes brief, minor discomfort, whereas a pot of hot oil yields severe burns. Both the drop and the pot of oil are at the same temperature (an intensive property), but the pot clearly contains much more heat (extensive property).

Note:

Hazard Diamond

You may have seen the symbol shown in [\[link\]](#) on containers of chemicals in a laboratory or workplace. Sometimes called a “fire diamond” or “hazard diamond,” this chemical hazard diamond provides valuable information that briefly summarizes the various dangers of which to be aware when working with a particular substance.



The National Fire Protection Agency (NFPA) hazard diamond summarizes the major hazards of a chemical substance.

The National Fire Protection Agency (NFPA) 704 Hazard Identification System was developed by NFPA to provide safety information about certain substances. The system details flammability, reactivity, health, and other hazards. Within the overall diamond symbol, the top (red) diamond specifies the level of fire hazard (temperature range for flash point). The blue (left) diamond indicates the level of health hazard. The yellow (right) diamond describes reactivity hazards, such as how readily the substance will undergo detonation or a violent chemical change. The white (bottom) diamond points out special hazards, such as if it is an oxidizer (which allows the substance to burn in the absence of air/oxygen), undergoes an unusual or dangerous reaction with water, is corrosive, acidic, alkaline, a biological hazard, radioactive, and so on. Each hazard is rated on a scale from 0 to 4, with 0 being no hazard and 4 being extremely hazardous.

While many elements differ dramatically in their chemical and physical properties, some elements have similar properties. We can identify sets of elements that exhibit common behaviors. For example, many elements conduct heat and electricity well, whereas others are poor conductors. These properties can be used to sort the elements into three classes: metals (elements that conduct well), nonmetals (elements that conduct poorly), and metalloids (elements that have properties of both metals and nonmetals).

The periodic table is a table of elements that places elements with similar properties close together ([link](#)). You will learn more about the periodic table as you continue your study of chemistry.

Period

Group

1

2

13

14

15

16

17

18

1	1	1.008	hydrogen																	2	4.003	helium																																												
2	3	6.94	lithium	4	9.012	beryllium																																																												
3	11	22.99	sodium	12	24.31	magnesium																																																												
4	19	39.10	potassium	20	40.08	calcium	21	44.96	scandium	22	47.87	titanium	23	50.94	vanadium	24	52.00	chromium	25	54.94	manganese	26	55.85	iron	27	58.93	cobalt	28	58.69	nickel	29	63.55	copper	30	65.38	zinc	31	69.72	gallium	32	72.63	germanium	33	74.92	arsenic	34	78.97	selenium	35	79.90	bromine	36	83.80	krypton												
5	37	85.47	rubidium	38	87.62	strontium	39	88.91	yttrium	40	91.22	zirconium	41	92.91	niobium	42	95.95	molybdenum	43	[97]	technetium	44	101.1	ruthenium	45	102.9	rhodium	46	106.4	palladium	47	107.9	silver	48	112.4	cadmium	49	114.8	indium	50	118.7	tin	51	121.8	antimony	52	127.6	tellurium	53	126.9	iodine	54	131.3	xenon												
6	55	132.9	cesium	56	137.3	barium	57-71	La-Lu	*	72	178.5	hafnium	73	180.9	tantalum	74	183.8	tungsten	75	186.2	rhenium	76	190.2	osmium	77	192.2	iridium	78	195.1	platinum	79	197.0	gold	80	200.6	mercury	81	204.4	thallium	82	207.2	lead	83	209.0	bismuth	84	[209]	polonium	85	[210]	astatine	86	[222]	radon												
7	87	[223]	francium	88	[226]	radium	89-103	Ac-Lr	**	104	[267]	rutherfordium	105	[270]	dubnium	106	[271]	seaborgium	107	[270]	bohrium	108	[277]	hassium	109	[276]	meitnerium	110	[281]	darmstadtium	111	[282]	roentgenium	112	[285]	copernicium	113	[285]	ununtrium	114	[289]	flerovium	115	[288]	ununpentium	116	[293]	livermorium	117	[294]	ununseptium	118	[294]	ununoctium												
							57	La	138.9	lanthanum	58	Ce	140.1	cerium	59	Pr	140.9	praseodymium	60	Nd	144.2	neodymium	61	Pm	[145]	promethium	62	Sm	150.4	samarium	63	Eu	152.0	europium	64	Gd	157.3	gadolinium	65	Tb	158.9	terbium	66	Dy	162.5	dysprosium	67	Ho	164.9	holmium	68	Er	167.3	erbium	69	Tm	168.9	thulium	70	Yb	173.1	ytterbium	71	Lu	175.0	lutetium
							89	Ac	[227]	actinium	90	Th	232.0	thorium	91	Pa	231.0	protactinium	92	U	238.0	uranium	93	Np	[237]	neptunium	94	Pu	[244]	plutonium	95	Am	[243]	americium	96	Cm	[247]	curium	97	Bk	[247]	berkelium	98	Cf	[251]	californium	99	Es	[252]	einsteinium	100	Fm	[257]	fermium	101	Md	[258]	mendelevium	102	No	[259]	nobelium	103	Lr	[262]	lawrencium

Atomic number → 1

Symbol → H

Atomic mass → 1.008

Name → hydrogen

Color Code

Metal

Metalloid

Nonmetal

Solid

Liquid

Gas

The periodic table shows how elements may be grouped according to certain similar properties. Note the background color denotes whether an element is a metal, metalloid, or nonmetal, whereas the element symbol color indicates whether it is a solid, liquid, or gas.

Key Concepts and Summary

All substances have distinct physical and chemical properties, and may undergo physical or chemical changes. Physical properties, such as hardness and boiling point, and physical changes, such as melting or freezing, do not involve a change in the composition of matter. Chemical properties, such as flammability and acidity, and chemical changes, such as rusting, involve production of matter that differs from that present beforehand.

Measurable properties fall into one of two categories. Extensive properties depend on the amount of matter present, for example, the mass of gold. Intensive properties do not depend on the amount of matter present, for example, the density of gold. Heat is an example of an extensive property, and temperature is an example of an intensive property.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Classify the six underlined properties in the following paragraph as chemical or physical:

Fluorine is a pale yellow gas that reacts with most substances. The free element melts at -220°C and boils at -188°C . Finely divided metals burn in fluorine with a bright flame. Nineteen grams of fluorine will react with 1.0 gram of hydrogen.

Exercise:

Problem:

Classify each of the following changes as physical or chemical:

- (a) condensation of steam
 - (b) burning of gasoline
 - (c) souring of milk
 - (d) dissolving of sugar in water
 - (e) melting of gold
-

Solution:

(a) physical; (b) chemical; (c) chemical; (d) physical; (e) physical

Exercise:

Problem:

Classify each of the following changes as physical or chemical:

- (a) coal burning
- (b) ice melting
- (c) mixing chocolate syrup with milk
- (d) explosion of a firecracker
- (e) magnetizing of a screwdriver

Exercise:

Problem:

The volume of a sample of oxygen gas changed from 10 mL to 11 mL as the temperature changed. Is this a chemical or physical change?

Solution:

physical

Exercise:

Problem:

A 2.0-liter volume of hydrogen gas combined with 1.0 liter of oxygen gas to produce 2.0 liters of water vapor. Does oxygen undergo a chemical or physical change?

Exercise:**Problem:**

Explain the difference between extensive properties and intensive properties.

Solution:

The value of an extensive property depends upon the amount of matter being considered, whereas the value of an intensive property is the same regardless of the amount of matter being considered.

Exercise:**Problem:**

Identify the following properties as either extensive or intensive.

- (a) volume
- (b) temperature
- (c) humidity
- (d) heat
- (e) boiling point

Exercise:**Problem:**

The density (d) of a substance is an intensive property that is defined as the ratio of its mass (m) to its volume (V).

Equation:

$$\text{density} = \frac{\text{mass}}{\text{volume}} \quad d = \frac{m}{V}$$

Considering that mass and volume are both extensive properties, explain why their ratio, density, is intensive.

Solution:

Being extensive properties, both mass and volume are directly proportional to the amount of substance under study. Dividing one extensive property by another will in effect “cancel” this dependence on amount, yielding a ratio that is independent of amount (an intensive property).

Glossary

chemical change

change producing a different kind of matter from the original kind of matter

chemical property

behavior that is related to the change of one kind of matter into another kind of matter

extensive property

property of a substance that depends on the amount of the substance

intensive property

property of a substance that is independent of the amount of the substance

physical change

change in the state or properties of matter that does not involve a change in its chemical composition

physical property

characteristic of matter that is not associated with any change in its chemical composition

Measurements

By the end of this section, you will be able to:

- Explain the process of measurement
- Identify the three basic parts of a quantity
- Describe the properties and units of length, mass, volume, density, temperature, and time
- Perform basic unit calculations and conversions in the metric and other unit systems

Measurements provide the macroscopic information that is the basis of most of the hypotheses, theories, and laws that describe the behavior of matter and energy in both the macroscopic and microscopic domains of chemistry. Every measurement provides three kinds of information: the size or magnitude of the measurement (a number); a standard of comparison for the measurement (a unit); and an indication of the uncertainty of the measurement. While the number and unit are explicitly represented when a quantity is written, the uncertainty is an aspect of the measurement result that is more implicitly represented and will be discussed later.

The number in the measurement can be represented in different ways, including decimal form and scientific notation. (Scientific notation is also known as exponential notation; a review of this topic can be found in [Appendix B](#).) For example, the maximum takeoff weight of a Boeing 777-200ER airliner is 298,000 kilograms, which can also be written as 2.98×10^5 kg. The mass of the average mosquito is about 0.0000025 kilograms, which can be written as 2.5×10^{-6} kg.

Units, such as liters, pounds, and centimeters, are standards of comparison for measurements. When we buy a 2-liter bottle of a soft drink, we expect that the volume of the drink was measured, so it is two times larger than the volume that everyone agrees to be 1 liter. The meat used to prepare a 0.25-pound hamburger is measured so it weighs one-fourth as much as 1 pound. Without units, a number can be meaningless, confusing, or possibly life threatening. Suppose a doctor prescribes phenobarbital to control a patient's seizures and states a dosage of "100" without specifying units. Not only will this be confusing to the medical professional giving the dose, but the consequences can be dire: 100 mg given three times per day can be

effective as an anticonvulsant, but a single dose of 100 g is more than 10 times the lethal amount.

We usually report the results of scientific measurements in SI units, an updated version of the metric system, using the units listed in [\[link\]](#). Other units can be derived from these base units. The standards for these units are fixed by international agreement, and they are called the **International System of Units** or **SI Units** (from the French, *Le Système International d'Unités*). SI units have been used by the United States National Institute of Standards and Technology (NIST) since 1964.

Base Units of the SI System		
Property Measured	Name of Unit	Symbol of Unit
length	meter	m
mass	kilogram	kg
time	second	s
temperature	kelvin	K
electric current	ampere	A
amount of substance	mole	mol
luminous intensity	candela	cd

Sometimes we use units that are fractions or multiples of a base unit. Ice cream is sold in quarts (a familiar, non-SI base unit), pints (0.5 quart), or gallons (4 quarts). We also use fractions or multiples of units in the SI

system, but these fractions or multiples are always powers of 10. Fractional or multiple SI units are named using a prefix and the name of the base unit. For example, a length of 1000 meters is also called a kilometer because the prefix *kilo* means “one thousand,” which in scientific notation is 10^3 (1 kilometer = 1000 m = 10^3 m). The prefixes used and the powers to which 10 are raised are listed in [\[link\]](#).

Common Unit Prefixes			
Prefix	Symbol	Factor	Example
femto	f	10^{-15}	1 femtosecond (fs) = 1×10^{-15} s (0.000000000000001 s)
pico	p	10^{-12}	1 picometer (pm) = 1×10^{-12} m (0.000000000001 m)
nano	n	10^{-9}	4 nanograms (ng) = 4×10^{-9} g (0.000000004 g)
micro	μ	10^{-6}	1 microliter (μ L) = 1×10^{-6} L (0.000001 L)
milli	m	10^{-3}	2 millimoles (mmol) = 2×10^{-3} mol (0.002 mol)
centi	c	10^{-2}	7 centimeters (cm) = 7×10^{-2} m (0.07 m)
deci	d	10^{-1}	1 deciliter (dL) = 1×10^{-1} L (0.1 L)

Common Unit Prefixes			
Prefix	Symbol	Factor	Example
kilo	k	10^3	1 kilometer (km) = 1×10^3 m (1000 m)
mega	M	10^6	3 megahertz (MHz) = 3×10^6 Hz (3,000,000 Hz)
giga	G	10^9	8 gigayears (Gyr) = 8×10^9 yr (8,000,000,000 yr)
tera	T	10^{12}	5 terawatts (TW) = 5×10^{12} W (5,000,000,000,000 W)

Note:



Need a refresher or more practice with scientific notation? Visit this [site](#) to go over the basics of scientific notation.

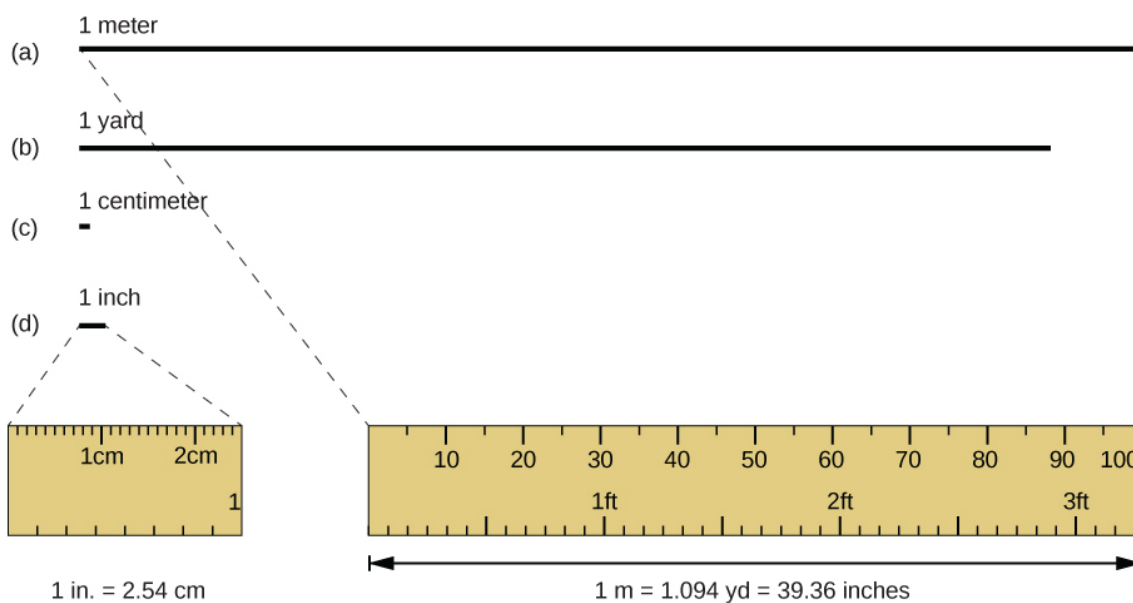
SI Base Units

The initial units of the metric system, which eventually evolved into the SI system, were established in France during the French Revolution. The original standards for the meter and the kilogram were adopted there in

1799 and eventually by other countries. This section introduces four of the SI base units commonly used in chemistry. Other SI units will be introduced in subsequent chapters.

Length

The standard unit of **length** in both the SI and original metric systems is the **meter (m)**. A meter was originally specified as 1/10,000,000 of the distance from the North Pole to the equator. It is now defined as the distance light in a vacuum travels in 1/299,792,458 of a second. A meter is about 3 inches longer than a yard ([link](#)); one meter is about 39.37 inches or 1.094 yards. Longer distances are often reported in kilometers ($1 \text{ km} = 1000 \text{ m} = 10^3 \text{ m}$), whereas shorter distances can be reported in centimeters ($1 \text{ cm} = 0.01 \text{ m} = 10^{-2} \text{ m}$) or millimeters ($1 \text{ mm} = 0.001 \text{ m} = 10^{-3} \text{ m}$).



The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd.

Mass

The standard unit of mass in the SI system is the **kilogram (kg)**. A kilogram was originally defined as the mass of a liter of water (a cube of water with an edge length of exactly 0.1 meter). It is now defined by a certain cylinder of platinum-iridium alloy, which is kept in France ([\[link\]](#)). Any object with the same mass as this cylinder is said to have a mass of 1 kilogram. One kilogram is about 2.2 pounds. The gram (g) is exactly equal to 1/1000 of the mass of the kilogram (10^{-3} kg).



This replica prototype kilogram is housed at the National Institute of Standards and Technology (NIST) in Maryland. (credit: National

Institutes of Standards and Technology)

Temperature

Temperature is an intensive property. The SI unit of temperature is the **kelvin (K)**. The IUPAC convention is to use kelvin (all lowercase) for the word, K (uppercase) for the unit symbol, and neither the word “degree” nor the degree symbol (°). The degree **Celsius (°C)** is also allowed in the SI system, with both the word “degree” and the degree symbol used for Celsius measurements. Celsius degrees are the same magnitude as those of kelvin, but the two scales place their zeros in different places. Water freezes at 273.15 K (0 °C) and boils at 373.15 K (100 °C) by definition, and normal human body temperature is approximately 310 K (37 °C). The conversion between these two units and the Fahrenheit scale will be discussed later in this chapter.

Time

The SI base unit of time is the **second (s)**. Small and large time intervals can be expressed with the appropriate prefixes; for example, 3 microseconds = 0.000003 s = 3×10^{-6} and 5 megaseconds = 5,000,000 s = 5×10^6 s. Alternatively, hours, days, and years can be used.

Derived SI Units

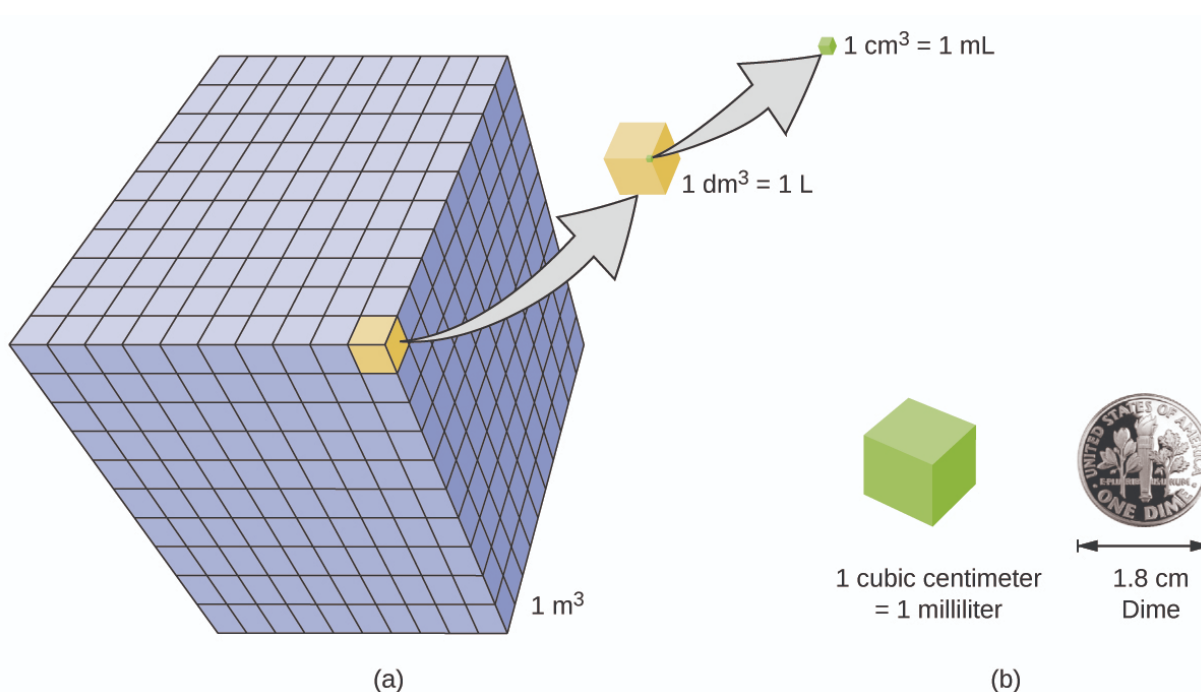
We can derive many units from the seven SI base units. For example, we can use the base unit of length to define a unit of volume, and the base units of mass and length to define a unit of density.

Volume

Volume is the measure of the amount of space occupied by an object. The standard SI unit of volume is defined by the base unit of length ([link](#)). The standard volume is a **cubic meter (m^3)**, a cube with an edge length of exactly one meter. To dispense a cubic meter of water, we could build a cubic box with edge lengths of exactly one meter. This box would hold a cubic meter of water or any other substance.

A more commonly used unit of volume is derived from the decimeter (0.1 m, or 10 cm). A cube with edge lengths of exactly one decimeter contains a volume of one cubic decimeter (dm^3). A **liter (L)** is the more common name for the cubic decimeter. One liter is about 1.06 quarts.

A **cubic centimeter (cm^3)** is the volume of a cube with an edge length of exactly one centimeter. The abbreviation **cc** (for **cubic centimeter**) is often used by health professionals. A cubic centimeter is also called a **milliliter (mL)** and is 1/1000 of a liter.



- (a) The relative volumes are shown for cubes of 1 m^3 , 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube.

Density

We use the mass and volume of a substance to determine its density. Thus, the units of density are defined by the base units of mass and length.

The **density** of a substance is the ratio of the mass of a sample of the substance to its volume. The SI unit for density is the kilogram per cubic meter (kg/m^3). For many situations, however, this is an inconvenient unit, and we often use grams per cubic centimeter (g/cm^3) for the densities of solids and liquids, and grams per liter (g/L) for gases. Although there are exceptions, most liquids and solids have densities that range from about 0.7 g/cm^3 (the density of gasoline) to 19 g/cm^3 (the density of gold). The density of air is about 1.2 g/L . [\[link\]](#) shows the densities of some common substances.

Densities of Common Substances		
Solids	Liquids	Gases (at 25 °C and 1 atm)
ice (at 0 °C) 0.92 g/cm^3	water 1.0 g/cm^3	dry air 1.20 g/L
oak (wood) $0.60\text{--}0.90 \text{ g/cm}^3$	ethanol 0.79 g/cm^3	oxygen 1.31 g/L
iron 7.9 g/cm^3	acetone 0.79 g/cm^3	nitrogen 1.14 g/L

Densities of Common Substances		
Solids	Liquids	Gases (at 25 °C and 1 atm)
copper 9.0 g/cm ³	glycerin 1.26 g/cm ³	carbon dioxide 1.80 g/L
lead 11.3 g/cm ³	olive oil 0.92 g/cm ³	helium 0.16 g/L
silver 10.5 g/cm ³	gasoline 0.70–0.77 g/cm ³	neon 0.83 g/L
gold 19.3 g/cm ³	mercury 13.6 g/cm ³	radon 9.1 g/L

While there are many ways to determine the density of an object, perhaps the most straightforward method involves separately finding the mass and volume of the object, and then dividing the mass of the sample by its volume. In the following example, the mass is found directly by weighing, but the volume is found indirectly through length measurements.

Equation:

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

Example:

Calculation of Density

Gold—in bricks, bars, and coins—has been a form of currency for centuries. In order to swindle people into paying for a brick of gold without actually investing in a brick of gold, people have considered filling the centers of hollow gold bricks with lead to fool buyers into thinking that the entire brick is gold. It does not work: Lead is a dense substance, but its

density is not as great as that of gold, 19.3 g/cm^3 . What is the density of lead if a cube of lead has an edge length of 2.00 cm and a mass of 90.7 g ?

Solution

The density of a substance can be calculated by dividing its mass by its volume. The volume of a cube is calculated by cubing the edge length.

Equation:

$$\text{volume of lead cube} = 2.00 \text{ cm} \times 2.00 \text{ cm} \times 2.00 \text{ cm} = 8.00 \text{ cm}^3$$

Equation:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{90.7 \text{ g}}{8.00 \text{ cm}^3} = \frac{11.3 \text{ g}}{1.00 \text{ cm}^3} = 11.3 \text{ g/cm}^3$$

(We will discuss the reason for rounding to the first decimal place in the next section.)

Check Your Learning

(a) To three decimal places, what is the volume of a cube (cm^3) with an edge length of 0.843 cm ?

(b) If the cube in part (a) is copper and has a mass of 5.34 g , what is the density of copper to two decimal places?

Note:

Answer:

(a) 0.599 cm^3 ; (b) 8.91 g/cm^3

Note:



To learn more about the relationship between mass, volume, and density, use this [interactive simulator](#) to explore the density of different materials, like wood, ice, brick, and aluminum.

Example:**Using Displacement of Water to Determine Density**

This [PhET simulation](#) illustrates another way to determine density, using displacement of water. Determine the density of the red and yellow blocks.

Solution

When you open the density simulation and select Same Mass, you can choose from several 5.00-kg colored blocks that you can drop into a tank containing 100.00 L water. The yellow block floats (it is less dense than water), and the water level rises to 105.00 L. While floating, the yellow block displaces 5.00 L water, an amount equal to the weight of the block. The red block sinks (it is more dense than water, which has density = 1.00 kg/L), and the water level rises to 101.25 L.

The red block therefore displaces 1.25 L water, an amount equal to the volume of the block. The density of the red block is:

Equation:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{5.00 \text{ kg}}{1.25 \text{ L}} = 4.00 \text{ kg/L}$$

Note that since the yellow block is not completely submerged, you cannot determine its density from this information. But if you hold the yellow block on the bottom of the tank, the water level rises to 110.00 L, which means that it now displaces 10.00 L water, and its density can be found:

Equation:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{5.00 \text{ kg}}{10.00 \text{ L}} = 0.500 \text{ kg/L}$$

Check Your Learning

Remove all of the blocks from the water and add the green block to the tank of water, placing it approximately in the middle of the tank.

Determine the density of the green block.

Note:

Answer:

2.00 kg/L

Key Concepts and Summary

Measurements provide quantitative information that is critical in studying and practicing chemistry. Each measurement has an amount, a unit for comparison, and an uncertainty. Measurements can be represented in either decimal or scientific notation. Scientists primarily use the SI (International System) or metric systems. We use base SI units such as meters, seconds, and kilograms, as well as derived units, such as liters (for volume) and g/cm^3 (for density). In many cases, we find it convenient to use unit prefixes that yield fractional and multiple units, such as microseconds (10^{-6} seconds) and megahertz (10^6 hertz), respectively.

Key Equations

- $\text{density} = \frac{\text{mass}}{\text{volume}}$

Chemistry End of Chapter Exercises

Exercise:

Problem: Is one liter about an ounce, a pint, a quart, or a gallon?

Exercise:

Problem: Is a meter about an inch, a foot, a yard, or a mile?

Solution:

about a yard

Exercise:

Problem:

Indicate the SI base units or derived units that are appropriate for the following measurements:

- (a) the length of a marathon race (26 miles 385 yards)
- (b) the mass of an automobile
- (c) the volume of a swimming pool
- (d) the speed of an airplane
- (e) the density of gold
- (f) the area of a football field
- (g) the maximum temperature at the South Pole on April 1, 1913

Exercise:

Problem:

Indicate the SI base units or derived units that are appropriate for the following measurements:

- (a) the mass of the moon

- (b) the distance from Dallas to Oklahoma City
 - (c) the speed of sound
 - (d) the density of air
 - (e) the temperature at which alcohol boils
 - (f) the area of the state of Delaware
 - (g) the volume of a flu shot or a measles vaccination
-

Solution:

(a) kilograms; (b) meters; (c) kilometers/second; (d) kilograms/cubic meter; (e) kelvin; (f) square meters; (g) cubic meters

Exercise:

Problem:

Give the name and symbol of the prefixes used with SI units to indicate multiplication by the following exact quantities.

- (a) 10^3
- (b) 10^{-2}
- (c) 0.1
- (d) 10^{-3}
- (e) 1,000,000
- (f) 0.000001

Exercise:

Problem:

Give the name of the prefix and the quantity indicated by the following symbols that are used with SI base units.

- (a) c
 - (b) d
 - (c) G
 - (d) k
 - (e) m
 - (f) n
 - (g) p
 - (h) T
-

Solution:

(a) centi-, $\times 10^{-2}$; (b) deci-, $\times 10^{-1}$; (c) Giga-, $\times 10^9$; (d) kilo-, $\times 10^3$; (e) milli-, $\times 10^{-3}$; (f) nano-, $\times 10^{-9}$; (g) pico-, $\times 10^{-12}$; (h) tera-, $\times 10^{12}$

Exercise:**Problem:**

A large piece of jewelry has a mass of 132.6 g. A graduated cylinder initially contains 48.6 mL water. When the jewelry is submerged in the graduated cylinder, the total volume increases to 61.2 mL.

- (a) Determine the density of this piece of jewelry.
- (b) Assuming that the jewelry is made from only one substance, what substance is it likely to be? Explain.

Exercise:**Problem:**

Visit this [PhET density simulation](#) and select the Same Volume Blocks.

- (a) What are the mass, volume, and density of the yellow block?
 - (b) What are the mass, volume and density of the red block?
 - (c) List the block colors in order from smallest to largest mass.
 - (d) List the block colors in order from lowest to highest density.
 - (e) How are mass and density related for blocks of the same volume?
-

Solution:

(a) 8.00 kg, 5.00 L, 1.60 kg/L; (b) 2.00 kg, 5.00 L, 0.400 kg/L; (c) red < green < blue < yellow; (d) If the volumes are the same, then the density is directly proportional to the mass.

Exercise:**Problem:**

Visit this [PhET density simulation](#) and select Custom Blocks and then My Block.

- (a) Enter mass and volume values for the block such that the mass in kg is *less than* the volume in L. What does the block do? Why? Is this always the case when mass < volume?
- (b) Enter mass and volume values for the block such that the mass in kg is *more than* the volume in L. What does the block do? Why? Is this always the case when mass > volume?
- (c) How would (a) and (b) be different if the liquid in the tank were ethanol instead of water?

(d) How would (a) and (b) be different if the liquid in the tank were mercury instead of water?

Exercise:

Problem:

Visit this [PhET density simulation](#) and select Mystery Blocks.

(a) Pick one of the Mystery Blocks and determine its mass, volume, density, and its likely identity.

(b) Pick a different Mystery Block and determine its mass, volume, density, and its likely identity.

(c) Order the Mystery Blocks from least dense to most dense. Explain.

Solution:

(a) (b) Answer is one of the following. A/yellow: mass = 65.14 kg, volume = 3.38 L, density = 19.3 kg/L, likely identity = gold. B/blue: mass = 0.64 kg, volume = 1.00 L, density = 0.64 kg/L, likely identity = apple. C/green: mass = 4.08 kg, volume = 5.83 L, density = 0.700 kg/L, likely identity = gasoline. D/red: mass = 3.10 kg, volume = 3.38 L, density = 0.920 kg/L, likely identity = ice; and E/purple: mass = 3.53 kg, volume = 1.00 L, density = 3.53 kg/L, likely identity = diamond. (c) B/blue/apple (0.64 kg/L) < C/green/gasoline (0.700 kg/L) < D/red/ice (0.920 kg/L) < E/purple/diamond (3.53 kg/L) < A/yellow/gold (19.3 kg/L)

Glossary

Celsius (°C)

unit of temperature; water freezes at 0 °C and boils at 100 °C on this scale

cubic centimeter (cm³ or cc)

volume of a cube with an edge length of exactly 1 cm

cubic meter (m³)
SI unit of volume

density
ratio of mass to volume for a substance or object

kelvin (K)
SI unit of temperature; 273.15 K = 0 °C

kilogram (kg)
standard SI unit of mass; 1 kg = approximately 2.2 pounds

length
measure of one dimension of an object

liter (L)
(also, cubic decimeter) unit of volume; 1 L = 1,000 cm³

meter (m)
standard metric and SI unit of length; 1 m = approximately 1.094 yards

milliliter (mL)
1/1,000 of a liter; equal to 1 cm³

second (s)
SI unit of time

SI units (International System of Units)
standards fixed by international agreement in the International System of Units (*Le Système International d'Unités*)

unit
standard of comparison for measurements

volume
amount of space occupied by an object

Measurement Uncertainty, Accuracy, and Precision

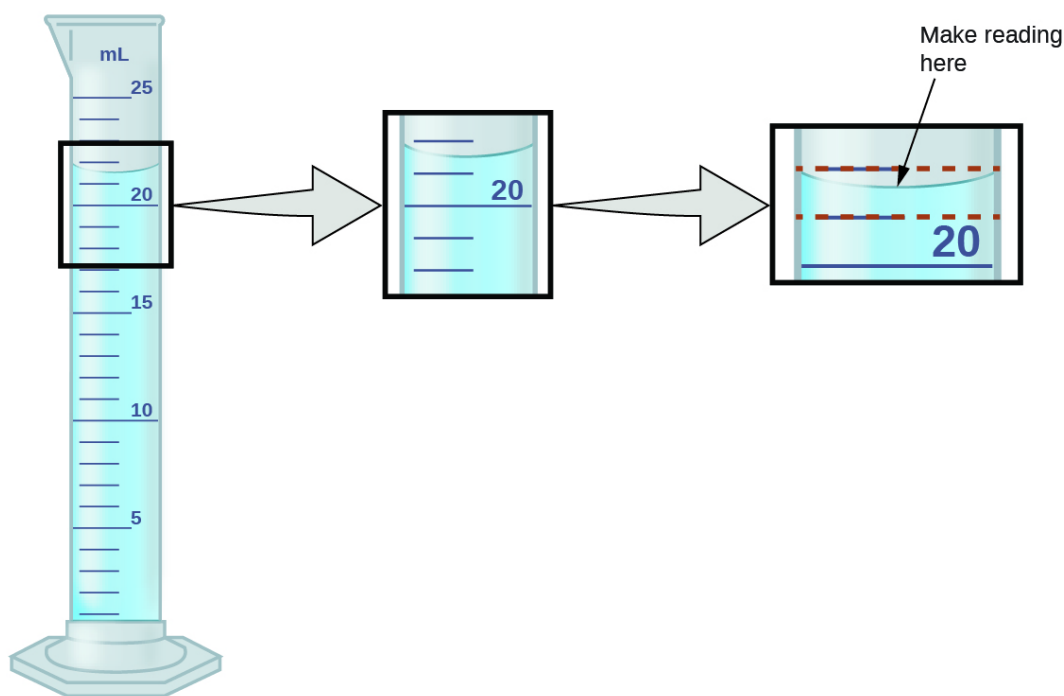
By the end of this section, you will be able to:

- Define accuracy and precision
- Distinguish exact and uncertain numbers
- Correctly represent uncertainty in quantities using significant figures
- Apply proper rounding rules to computed quantities

Counting is the only type of measurement that is free from uncertainty, provided the number of objects being counted does not change while the counting process is underway. The result of such a counting measurement is an example of an **exact number**. If we count eggs in a carton, we know *exactly* how many eggs the carton contains. The numbers of defined quantities are also exact. By definition, 1 foot is exactly 12 inches, 1 inch is exactly 2.54 centimeters, and 1 gram is exactly 0.001 kilogram. Quantities derived from measurements other than counting, however, are uncertain to varying extents due to practical limitations of the measurement process used.

Significant Figures in Measurement

The numbers of measured quantities, unlike defined or directly counted quantities, are not exact. To measure the volume of liquid in a graduated cylinder, you should make a reading at the bottom of the meniscus, the lowest point on the curved surface of the liquid.

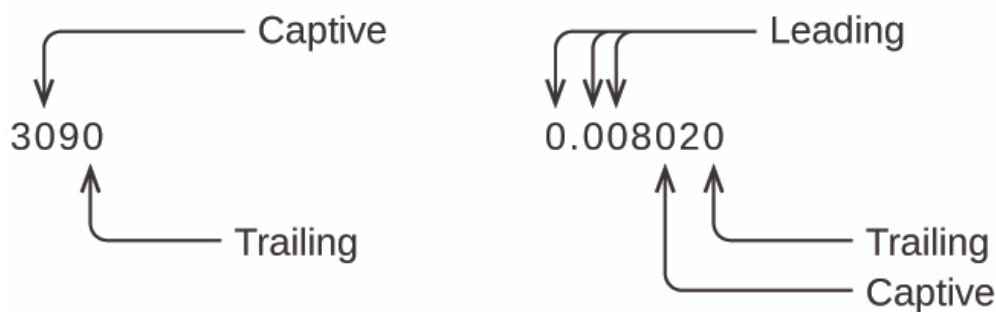


To measure the volume of liquid in this graduated cylinder, you must mentally subdivide the distance between the 21 and 22 mL marks into tenths of a milliliter, and then make a reading (estimate) at the bottom of the meniscus.

Refer to the illustration in [\[link\]](#). The bottom of the meniscus in this case clearly lies between the 21 and 22 markings, meaning the liquid volume is *certainly* greater than 21 mL but less than 22 mL. The meniscus appears to be a bit closer to the 22-mL mark than to the 21-mL mark, and so a reasonable estimate of the liquid's volume would be 21.6 mL. In the number 21.6, then, the digits 2 and 1 are certain, but the 6 is an estimate. Some people might estimate the meniscus position to be equally distant from each of the markings and estimate the tenth-place digit as 5, while others may think it to be even closer to the 22-mL mark and estimate this digit to be 7. Note that it would be pointless to attempt to estimate a digit for the hundredths place, given that the tenths-place digit is uncertain. In general, numerical scales such as the one on this graduated cylinder will permit measurements to one-tenth of the smallest scale division. The scale in this case has 1-mL divisions, and so volumes may be measured to the nearest 0.1 mL.

This concept holds true for all measurements, even if you do not actively make an estimate. If you place a quarter on a standard electronic balance, you may obtain a reading of 6.72 g. The digits 6 and 7 are certain, and the 2 indicates that the mass of the quarter is likely between 6.71 and 6.73 grams. The quarter weighs *about* 6.72 grams, with a nominal uncertainty in the measurement of ± 0.01 gram. If we weigh the quarter on a more sensitive balance, we may find that its mass is 6.723 g. This means its mass lies between 6.722 and 6.724 grams, an uncertainty of 0.001 gram. Every measurement has some **uncertainty**, which depends on the device used (and the user's ability). All of the digits in a measurement, including the uncertain last digit, are called **significant figures** or **significant digits**. Note that zero may be a measured value; for example, if you stand on a scale that shows weight to the nearest pound and it shows "120," then the 1 (hundreds), 2 (tens) and 0 (ones) are all significant (measured) values.

Whenever you make a measurement properly, all the digits in the result are significant. But what if you were analyzing a reported value and trying to determine what is significant and what is not? Well, for starters, all nonzero digits are significant, and it is only zeros that require some thought. We will use the terms "leading," "trailing," and "captive" for the zeros and will consider how to deal with them.



Starting with the first nonzero digit on the left, count this digit and all remaining digits to the right. This is the number of significant figures in the measurement unless the last digit is a trailing zero lying to the left of the decimal point.

First nonzero figure on the left
1267 m
Four significant figures

First nonzero figure on the left
55.0 g
Three significant figures: note that the zero is to the right of the decimal point and therefore a significant figure

Captive zeros result from measurement and are therefore always significant. Leading zeros, however, are never significant—they merely tell us where the decimal point is located.

First nonzero figure on the left
70.607 mL
Five significant figures: all figures are measured including the two zeros

First nonzero figure on the left
0.00832407 mL
Six significant figures

The leading zeros in this example are not significant. We could use exponential notation (as described in Appendix B) and express the number as 8.32407×10^{-3} ; then the number 8.32407 contains all of the significant figures, and 10^{-3} locates the decimal point.

The number of significant figures is uncertain in a number that ends with a zero to the left of the decimal point location. The zeros in the measurement 1,300 grams could be significant or they could simply indicate where the decimal point is located. The ambiguity can be resolved with the use of exponential notation: 1.3×10^3 (two significant figures), 1.30×10^3 (three significant figures, if the tens place was measured), or 1.300×10^3 (four significant figures, if the ones place was also measured). In cases where only the decimal-formatted number is available, it is prudent to assume that all trailing zeros are not significant.

Significant figures: clearly result of measurement
1300 g
These zeros could be significant (measured), or they could be placeholders

When determining significant figures, be sure to pay attention to reported values and think about the measurement and significant figures in terms of what is reasonable or likely when evaluating whether the value makes sense. For example, the official January 2014 census reported the resident population of the US as 317,297,725. Do you think the US population was correctly determined to the reported nine significant figures, that is, to the exact number of people? People are constantly being born, dying, or moving into or out of the country, and assumptions are made to account for the large number of people who are not actually counted. Because of these uncertainties, it might be more reasonable to expect that we know the population to within perhaps a million or so, in which case the population should be reported as 3.17×10^8 people.

Significant Figures in Calculations

A second important principle of uncertainty is that results calculated from a measurement are at least as uncertain as the measurement itself. We must take the uncertainty in our measurements into account to avoid misrepresenting the uncertainty in calculated results. One way to do this is to report the result of a calculation with the correct number of significant figures, which is determined by the following three rules for **rounding** numbers:

1. When we add or subtract numbers, we should round the result to the same number of decimal places as the number with the least number of decimal places (the least precise value in terms of addition and subtraction).
2. When we multiply or divide numbers, we should round the result to the same number of digits as the number with the least number of significant figures (the least precise value in terms of multiplication and division).
3. If the digit to be dropped (the one immediately to the right of the digit to be retained) is less than 5, we “round down” and leave the retained digit unchanged; if it is more than 5, we “round up” and increase the retained digit by 1; if the dropped digit is 5, we round up or down, whichever yields an even value for the retained digit. (The last part of this rule may strike you as a bit odd, but it’s based on reliable statistics and is aimed at avoiding any bias when dropping the digit “5,” since it is equally close to both possible values of the retained digit.)

The following examples illustrate the application of this rule in rounding a few different numbers to three significant figures:

- 0.028675 rounds “up” to 0.0287 (the dropped digit, 7, is greater than 5)
- 18.3384 rounds “down” to 18.3 (the dropped digit, 3, is less than 5)
- 6.8752 rounds “up” to 6.88 (the dropped digit is 5, and the retained digit is even)
- 92.85 rounds “down” to 92.8 (the dropped digit is 5, and the retained digit is even)

Let’s work through these rules with a few examples.

Example:

Rounding Numbers

Round the following to the indicated number of significant figures:

- (a) 31.57 (to two significant figures)
- (b) 8.1649 (to three significant figures)
- (c) 0.051065 (to four significant figures)
- (d) 0.90275 (to four significant figures)

Solution

- (a) 31.57 rounds “up” to 32 (the dropped digit is 5, and the retained digit is even)
- (b) 8.1649 rounds “down” to 8.16 (the dropped digit, 4, is less than 5)
- (c) 0.051065 rounds “down” to 0.05106 (the dropped digit is 5, and the retained digit is even)
- (d) 0.90275 rounds “up” to 0.9028 (the dropped digit is 5, and the retained digit is even)

Check Your Learning

Round the following to the indicated number of significant figures:

- (a) 0.424 (to two significant figures)
- (b) 0.0038661 (to three significant figures)
- (c) 421.25 (to four significant figures)
- (d) 28,683.5 (to five significant figures)

Note:

Answer:

(a) 0.42; (b) 0.00387; (c) 421.2; (d) 28,684

Example:

Addition and Subtraction with Significant Figures

Rule: When we add or subtract numbers, we should round the result to the same number of decimal places as the number with the least number of decimal places (i.e., the least precise value in terms of addition and subtraction).

(a) Add 1.0023 g and 4.383 g.

(b) Subtract 421.23 g from 486 g.

Solution

(a)

$$\begin{array}{r} 1.0023 \text{ g} \\ + 4.383 \text{ g} \\ \hline 5.3853 \text{ g} \end{array}$$

Answer is 5.385 g (round to the thousandths place; three decimal places)

(b)

$$\begin{array}{r} 486 \text{ g} \\ - 421.23 \text{ g} \\ \hline 64.77 \text{ g} \end{array}$$

Answer is 65 g (round to the ones place; no decimal places)

$$\begin{array}{r} 1.0023 \leftarrow \text{Ten thousandths place} \\ + 4.383 \leftarrow \text{Thousandths place: least precise} \\ \hline 5.3853 \end{array}$$

↑
Round to thousandths

(a)

$$\begin{array}{r} 486 \text{ g} \\ - 421.23 \text{ g} \\ \hline 64.77 \text{ g} \end{array} \longrightarrow \text{Answer is 65 g}$$

↑
Round to ones

(b)

Check Your Learning

(a) Add 2.334 mL and 0.31 mL.

(b) Subtract 55.8752 m from 56.533 m.

Note:

Answer:

(a) 2.64 mL; (b) 0.658 m

Example:**Multiplication and Division with Significant Figures**

Rule: When we multiply or divide numbers, we should round the result to the same number of digits as the number with the least number of significant figures (the least precise value in terms of multiplication and division).

(a) Multiply 0.6238 cm by 6.6 cm.

(b) Divide 421.23 g by 486 mL.

Solution

(a)

$0.6238 \text{ cm} \times 6.6 \text{ cm} = 4.11708 \text{ cm}^2 \rightarrow$ result is 4.1 cm^2 (round to two significant figures)
four significant figures \times two significant figures \rightarrow two significant figures answer

(b)

$\frac{421.23 \text{ g}}{486 \text{ mL}} = 0.86728... \text{ g/mL} \rightarrow$ result is 0.867 g/mL (round to three significant figures)

$\frac{\text{five significant figures}}{\text{three significant figures}} \rightarrow$ three significant figures answer

Check Your Learning

(a) Multiply 2.334 cm and 0.320 cm.

(b) Divide 55.8752 m by 56.53 s.

Note:**Answer:**

(a) 0.747 cm^2 (b) 0.9884 m/s

In the midst of all these technicalities, it is important to keep in mind the reason why we use significant figures and rounding rules—to correctly represent the certainty of the values we report and to ensure that a calculated result is not represented as being more certain than the least certain value used in the calculation.

Example:**Calculation with Significant Figures**

One common bathtub is 13.44 dm long, 5.920 dm wide, and 2.54 dm deep. Assume that the tub is rectangular and calculate its approximate volume in liters.

Solution**Equation:**

$$\begin{aligned} V &= l \times w \times d \\ &= 13.44 \text{ dm} \times 5.920 \text{ dm} \times 2.54 \text{ dm} \\ &= 202.09459... \text{ dm}^3 \text{ (value from calculator)} \\ &= 202 \text{ dm}^3, \text{ or } 202 \text{ L (answer rounded to three significant figures)} \end{aligned}$$

Check Your Learning

What is the density of a liquid with a mass of 31.1415 g and a volume of 30.13 cm³?

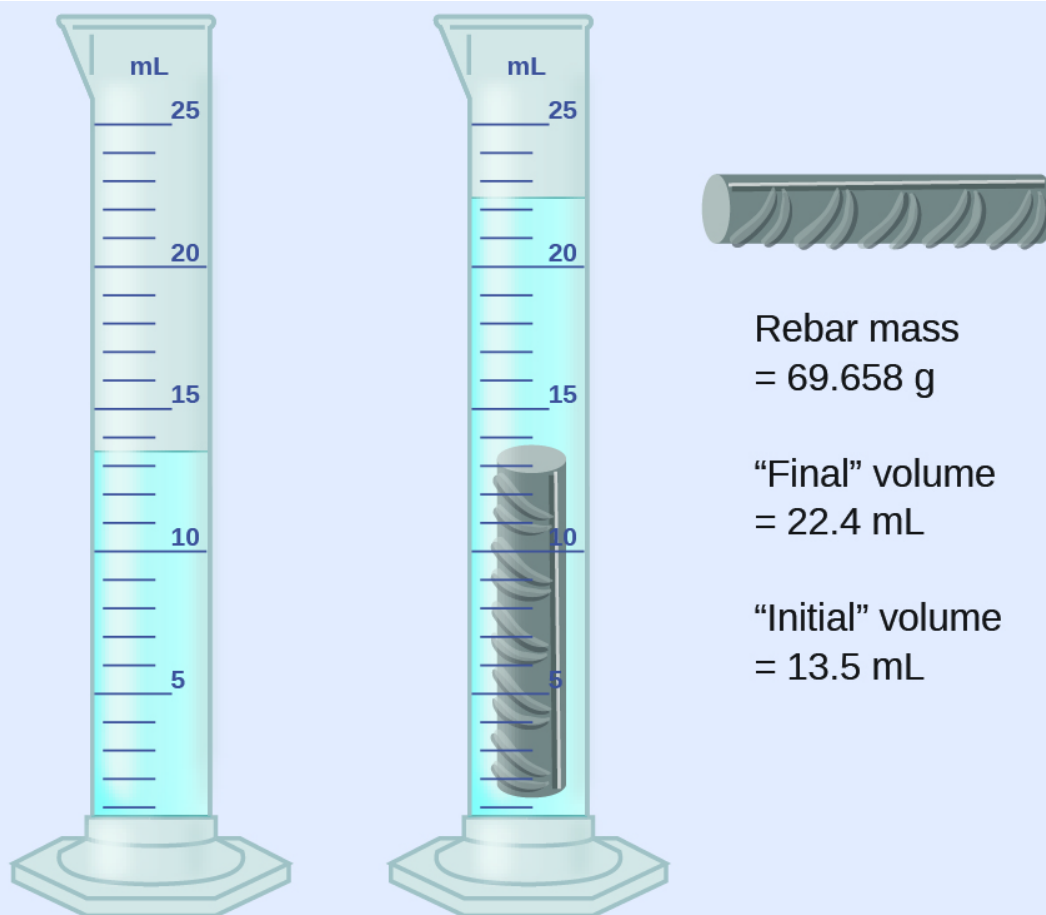
Note:

Answer:

1.034 g/mL

Example:**Experimental Determination of Density Using Water Displacement**

A piece of rebar is weighed and then submerged in a graduated cylinder partially filled with water, with results as shown.



(a) Use these values to determine the density of this piece of rebar.

(b) Rebar is mostly iron. Does your result in (a) support this statement? How?

Solution

The volume of the piece of rebar is equal to the volume of the water displaced:

Equation:

$$\text{volume} = 22.4 \text{ mL} - 13.5 \text{ mL} = 8.9 \text{ mL} = 8.9 \text{ cm}^3$$

(rounded to the nearest 0.1 mL, per the rule for addition and subtraction)

The density is the mass-to-volume ratio:

Equation:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{69.658 \text{ g}}{8.9 \text{ cm}^3} = 7.8 \text{ g/cm}^3$$

(rounded to two significant figures, per the rule for multiplication and division)

From [\[link\]](#), the density of iron is 7.9 g/cm^3 , very close to that of rebar, which lends some support to the fact that rebar is mostly iron.

Check Your Learning

An irregularly shaped piece of a shiny yellowish material is weighed and then submerged in a graduated cylinder, with results as shown.

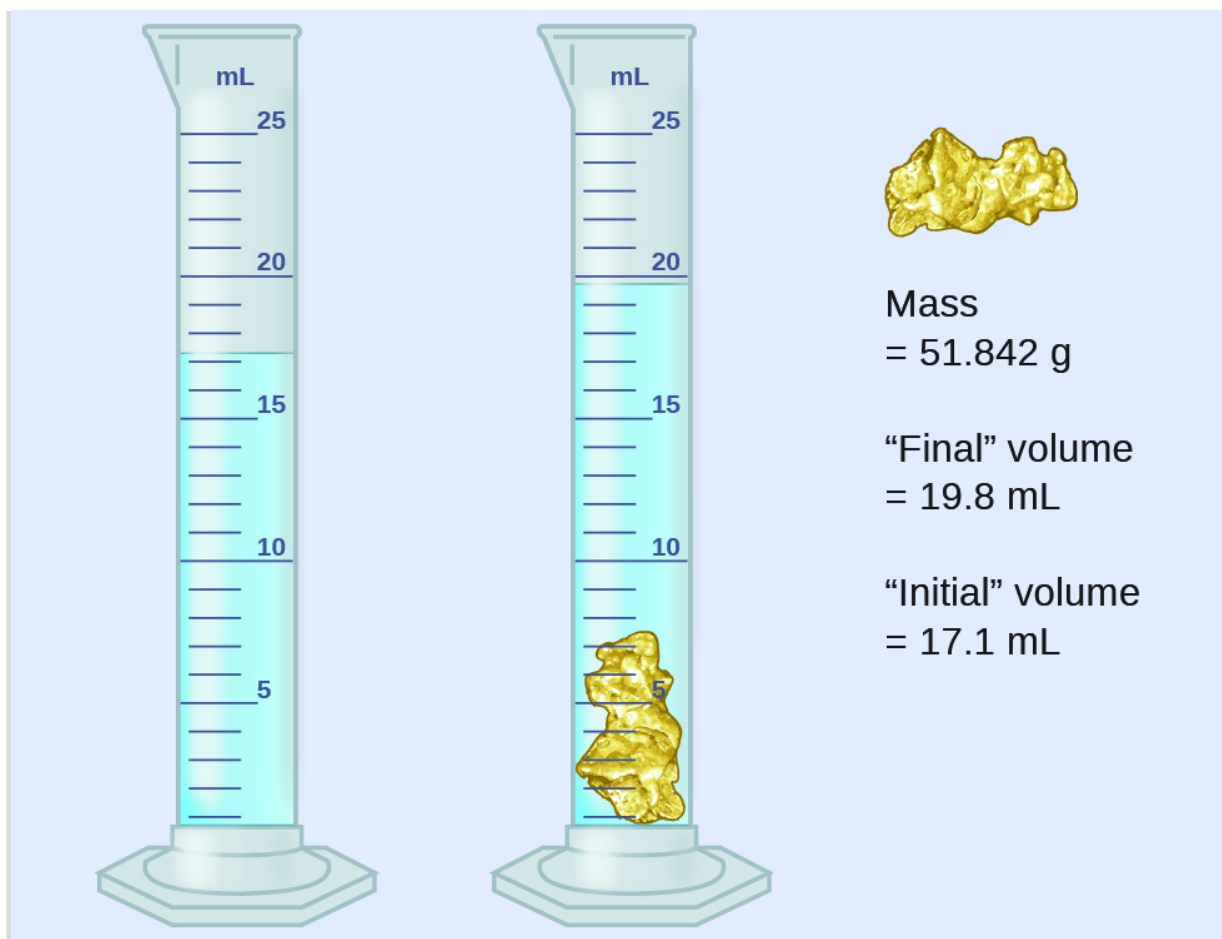


Diagram illustrating the measurement of the volume of an irregular solid (gold) using a graduated cylinder. The initial volume of water is 17.1 mL. After the gold is added, the final volume is 19.8 mL. The mass of the gold is 51.842 g.

Mass
= 51.842 g

“Final” volume
= 19.8 mL

“Initial” volume
= 17.1 mL

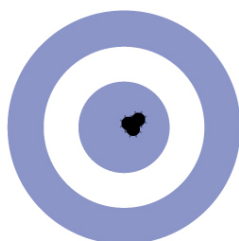
(a) Use these values to determine the density of this material.
(b) Do you have any reasonable guesses as to the identity of this material? Explain your reasoning.

Note:
Answer:
(a) 19 g/cm^3 ; (b) It is likely gold; the right appearance for gold and very close to the density given for gold in [\[link\]](#).

Accuracy and Precision

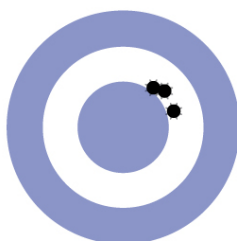
Scientists typically make repeated measurements of a quantity to ensure the quality of their findings and to know both the **precision** and the **accuracy** of their results. Measurements are said to be precise if they yield very similar results when repeated in the same manner. A measurement is considered accurate if it yields a result that is very close to the true or accepted value. Precise values

agree with each other; accurate values agree with a true value. These characterizations can be extended to other contexts, such as the results of an archery competition ([link](#)).



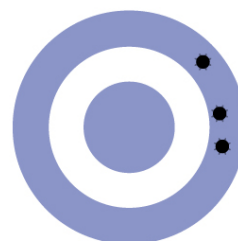
Accurate
and precise

(a)



Precise,
not accurate

(b)



Not accurate,
not precise

(c)

(a) These arrows are close to both the bull's eye and one another, so they are both accurate and precise. (b) These arrows are close to one another but not on target, so they are precise but not accurate. (c) These arrows are neither on target nor close to one another, so they are neither accurate nor precise.

Suppose a quality control chemist at a pharmaceutical company is tasked with checking the accuracy and precision of three different machines that are meant to dispense 10 ounces (296 mL) of cough syrup into storage bottles. She proceeds to use each machine to fill five bottles and then carefully determines the actual volume dispensed, obtaining the results tabulated in [link](#).

Volume (mL) of Cough Medicine Delivered by 10-oz (296 mL) Dispensers		
Dispenser #1	Dispenser #2	Dispenser #3
283.3	298.3	296.1
284.1	294.2	295.9
283.9	296.0	296.1
284.0	297.8	296.0
284.1	293.9	296.1

Considering these results, she will report that dispenser #1 is precise (values all close to one another, within a few tenths of a milliliter) but not accurate (none of the values are close to the target value of 296 mL, each being more than 10 mL too low). Results for dispenser #2 represent improved accuracy (each volume is less than 3 mL away from 296 mL) but worse precision (volumes vary by more than 4 mL). Finally, she can report that dispenser #3 is working well, dispensing cough syrup both accurately (all volumes within 0.1 mL of the target volume) and precisely (volumes differing from each other by no more than 0.2 mL).

Key Concepts and Summary

Quantities can be exact or measured. Measured quantities have an associated uncertainty that is represented by the number of significant figures in the measurement. The uncertainty of a calculated value depends on the uncertainties in the values used in the calculation and is reflected in how the value is rounded. Measured values can be accurate (close to the true value) and/or precise (showing little variation when measured repeatedly).

Chemistry End of Chapter Exercises

Exercise:

Problem:

Express each of the following numbers in scientific notation with correct significant figures:

- (a) 711.0
- (b) 0.239
- (c) 90743
- (d) 134.2
- (e) 0.05499
- (f) 10000.0
- (g) 0.000000738592

Exercise:

Problem:

Express each of the following numbers in exponential notation with correct significant figures:

- (a) 704
- (b) 0.03344
- (c) 547.9
- (d) 22086

(e) 1000.00

(f) 0.0000000651

(g) 0.007157

Solution:

(a) 7.04×10^2 ; (b) 3.344×10^{-2} ; (c) 5.479×10^2 ; (d) 2.2086×10^4 ; (e) 1.00000×10^3 ; (f) 6.51×10^{-8} ; (g) 7.157×10^{-3}

Exercise:

Problem:

Indicate whether each of the following can be determined exactly or must be measured with some degree of uncertainty:

- (a) the number of eggs in a basket
- (b) the mass of a dozen eggs
- (c) the number of gallons of gasoline necessary to fill an automobile gas tank
- (d) the number of cm in 2 m
- (e) the mass of a textbook
- (f) the time required to drive from San Francisco to Kansas City at an average speed of 53 mi/h

Exercise:

Problem:

Indicate whether each of the following can be determined exactly or must be measured with some degree of uncertainty:

- (a) the number of seconds in an hour
- (b) the number of pages in this book
- (c) the number of grams in your weight
- (d) the number of grams in 3 kilograms
- (e) the volume of water you drink in one day
- (f) the distance from San Francisco to Kansas City

Solution:

(a) exact; (b) exact; (c) uncertain; (d) exact; (e) uncertain; (f) uncertain

Exercise:

Problem: How many significant figures are contained in each of the following measurements?

- (a) 38.7 g
- (b) 2×10^{18} m
- (c) 3,486,002 kg
- (d) 9.74150×10^{-4} J
- (e) 0.0613 cm³
- (f) 17.0 kg
- (g) 0.01400 g/mL

Exercise:

Problem: How many significant figures are contained in each of the following measurements?

- (a) 53 cm
- (b) 2.05×10^8 m
- (c) 86,002 J
- (d) 9.740×10^4 m/s
- (e) 10.0613 m³
- (f) 0.17 g/mL
- (g) 0.88400 s

Solution:

(a) two; (b) three; (c) five; (d) four; (e) six; (f) two; (g) five

Exercise:

Problem:

The following quantities were reported on the labels of commercial products. Determine the number of significant figures in each.

- (a) 0.0055 g active ingredients
- (b) 12 tablets
- (c) 3% hydrogen peroxide
- (d) 5.5 ounces

- (e) 473 mL
- (f) 1.75% bismuth
- (g) 0.001% phosphoric acid
- (h) 99.80% inert ingredients

Exercise:

Problem: Round off each of the following numbers to two significant figures:

- (a) 0.436
 - (b) 9.000
 - (c) 27.2
 - (d) 135
 - (e) 1.497×10^{-3}
 - (f) 0.445
-

Solution:

(a) 0.44; (b) 9.0; (c) 27; (d) 140; (e) 1.5×10^{-3} ; (f) 0.44

Exercise:

Problem: Round off each of the following numbers to two significant figures:

- (a) 517
- (b) 86.3
- (c) 6.382×10^3
- (d) 5.0008
- (e) 22.497
- (f) 0.885

Exercise:

Problem:

Perform the following calculations and report each answer with the correct number of significant figures.

- (a) 628×342

(b) $(5.63 \times 10^2) \times (7.4 \times 10^3)$

(c) $\frac{28.0}{13.483}$

(d) 8119×0.000023

(e) $14.98 + 27,340 + 84.7593$

(f) $42.7 + 0.259$

Solution:

(a) 2.15×10^5 ; (b) 4.2×10^6 ; (c) 2.08; (d) 0.19; (e) 27,440; (f) 43.0

Exercise:

Problem:

Perform the following calculations and report each answer with the correct number of significant figures.

(a) 62.8×34

(b) $0.147 + 0.0066 + 0.012$

(c) $38 \times 95 \times 1.792$

(d) $15 - 0.15 - 0.6155$

(e) $8.78 \times \left(\frac{0.0500}{0.478} \right)$

(f) $140 + 7.68 + 0.014$

(g) $28.7 - 0.0483$

(h) $\frac{(88.5 - 87.57)}{45.13}$

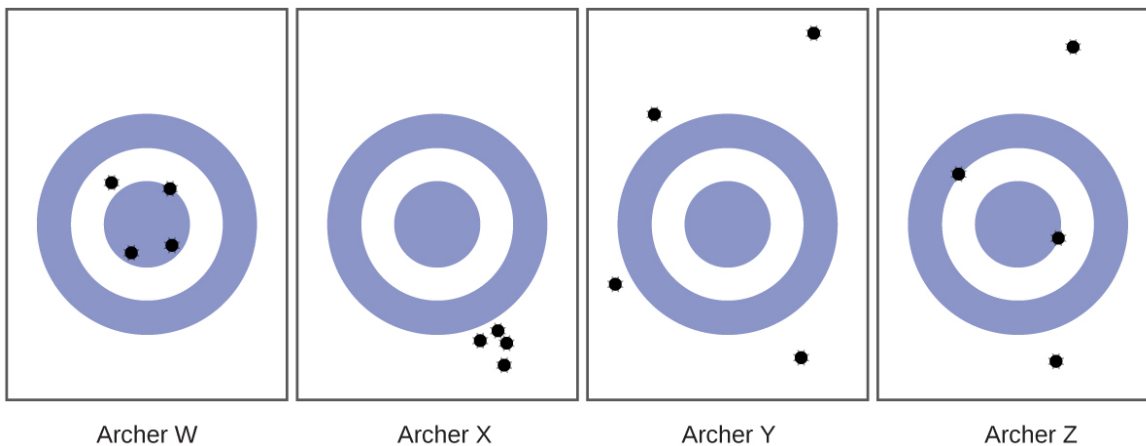
Exercise:

Problem: Consider the results of the archery contest shown in this figure.

(a) Which archer is most precise?

(b) Which archer is most accurate?

(c) Who is both least precise and least accurate?



Solution:

(a) Archer X; (b) Archer W; (c) Archer Y

Exercise:

Problem: Classify the following sets of measurements as accurate, precise, both, or neither.

(a) Checking for consistency in the weight of chocolate chip cookies: 17.27 g, 13.05 g, 19.46 g, 16.92 g

(b) Testing the volume of a batch of 25-mL pipettes: 27.02 mL, 26.99 mL, 26.97 mL, 27.01 mL

(c) Determining the purity of gold: 99.9999%, 99.9998%, 99.9998%, 99.9999%

Glossary

accuracy

how closely a measurement aligns with a correct value

exact number

number derived by counting or by definition

precision

how closely a measurement matches the same measurement when repeated

rounding

procedure used to ensure that calculated results properly reflect the uncertainty in the measurements used in the calculation

significant figures

(also, significant digits) all of the measured digits in a determination, including the uncertain last digit

uncertainty

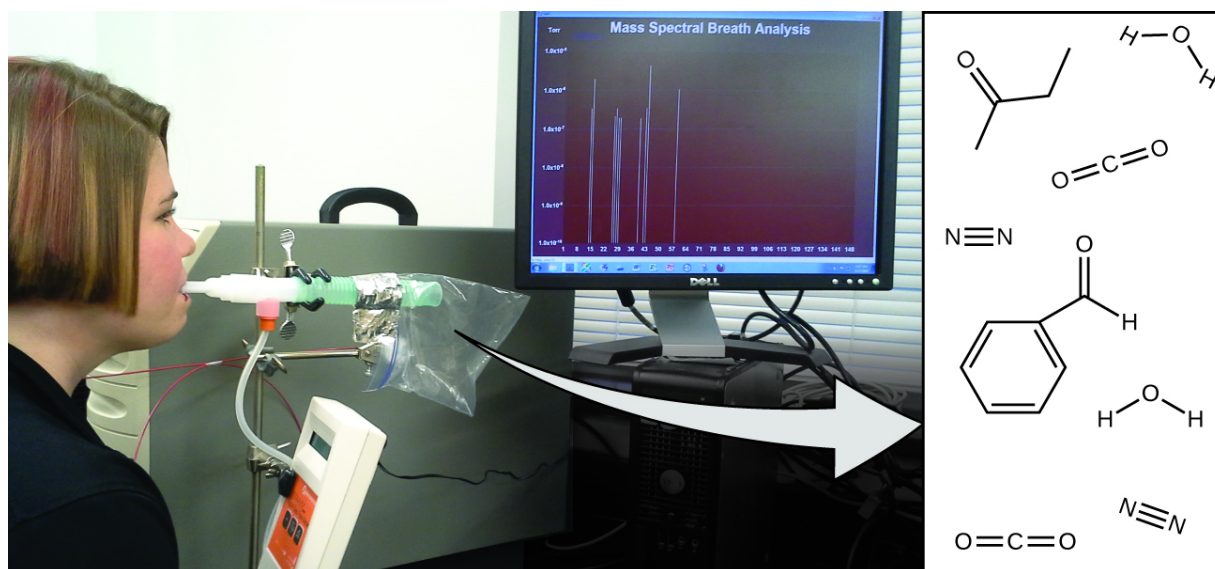
estimate of amount by which measurement differs from true value

Introduction

class="introduction"

- Early Ideas in Atomic Theory
- Evolution of Atomic Theory
- Atomic Structure and Symbolism
- Chemical Formulas
- The Periodic Table
- Molecular and Ionic Compounds
- Chemical Nomenclature

Analysis of
molecules in
an exhaled
breath can
provide
valuable
information,
leading to
early
diagnosis of
diseases or
detection of
environmenta
l exposure to
harmful
substances.
(credit:
modification
of work by
Paul Flowers)



Your overall health and susceptibility to disease depends upon the complex interaction between your genetic makeup and environmental exposure, with the outcome difficult to predict. Early detection of biomarkers, substances that indicate an organism's disease or physiological state, could allow diagnosis and treatment before a condition becomes serious or irreversible. Recent studies have shown that your exhaled breath can contain molecules that may be biomarkers for recent exposure to environmental contaminants or for pathological conditions ranging from asthma to lung cancer. Scientists are working to develop biomarker "fingerprints" that could be used to diagnose a specific disease based on the amounts and identities of certain molecules in a patient's exhaled breath. An essential concept underlying this goal is that of a molecule's identity, which is determined by the numbers and types of atoms it contains, and how they are bonded together. This chapter will describe some of the fundamental chemical principles related to the composition of matter, including those central to the concept of molecular identity.

Early Ideas in Atomic Theory

By the end of this section, you will be able to:

- State the postulates of Dalton's atomic theory
- Use postulates of Dalton's atomic theory to explain the laws of definite and multiple proportions

The language used in chemistry is seen and heard in many disciplines, ranging from medicine to engineering to forensics to art. The language of chemistry includes its own vocabulary as well as its own form of shorthand. Chemical symbols are used to represent atoms and elements. Chemical formulas depict molecules as well as the composition of compounds. Chemical equations provide information about the quality and quantity of the changes associated with chemical reactions.

This chapter will lay the foundation for our study of the language of chemistry. The concepts of this foundation include the atomic theory, the composition and mass of an atom, the variability of the composition of isotopes, ion formation, chemical bonds in ionic and covalent compounds, the types of chemical reactions, and the naming of compounds. We will also introduce one of the most powerful tools for organizing chemical knowledge: the periodic table.

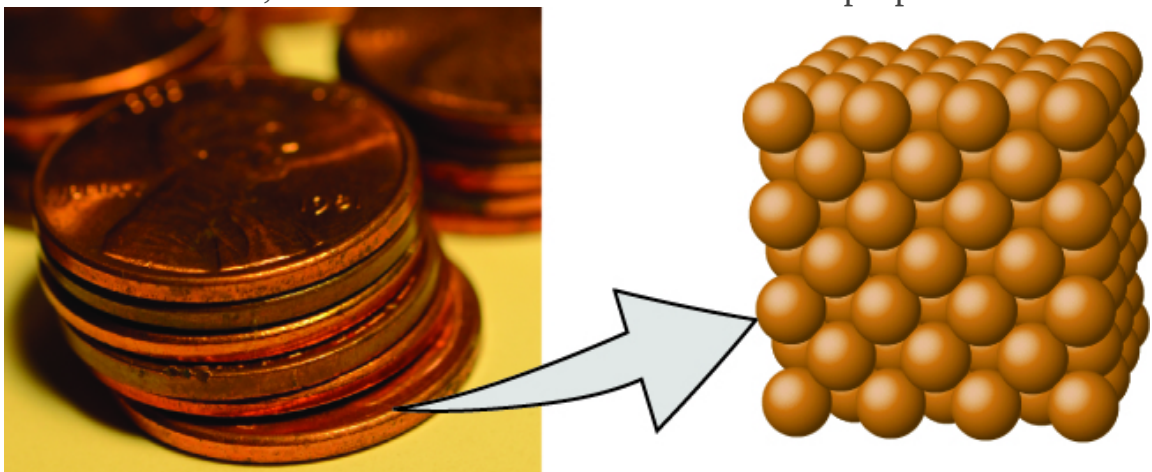
Atomic Theory through the Nineteenth Century

The earliest recorded discussion of the basic structure of matter comes from ancient Greek philosophers, the scientists of their day. In the fifth century BC, Leucippus and Democritus argued that all matter was composed of small, finite particles that they called *atomos*, a term derived from the Greek word for “indivisible.” They thought of atoms as moving particles that differed in shape and size, and which could join together. Later, Aristotle and others came to the conclusion that matter consisted of various combinations of the four “elements”—fire, earth, air, and water—and could be infinitely divided. Interestingly, these philosophers thought about atoms and “elements” as philosophical concepts, but apparently never considered performing experiments to test their ideas.

The Aristotelian view of the composition of matter held sway for over two thousand years, until English schoolteacher John Dalton helped to revolutionize chemistry with his hypothesis that the behavior of matter could be explained

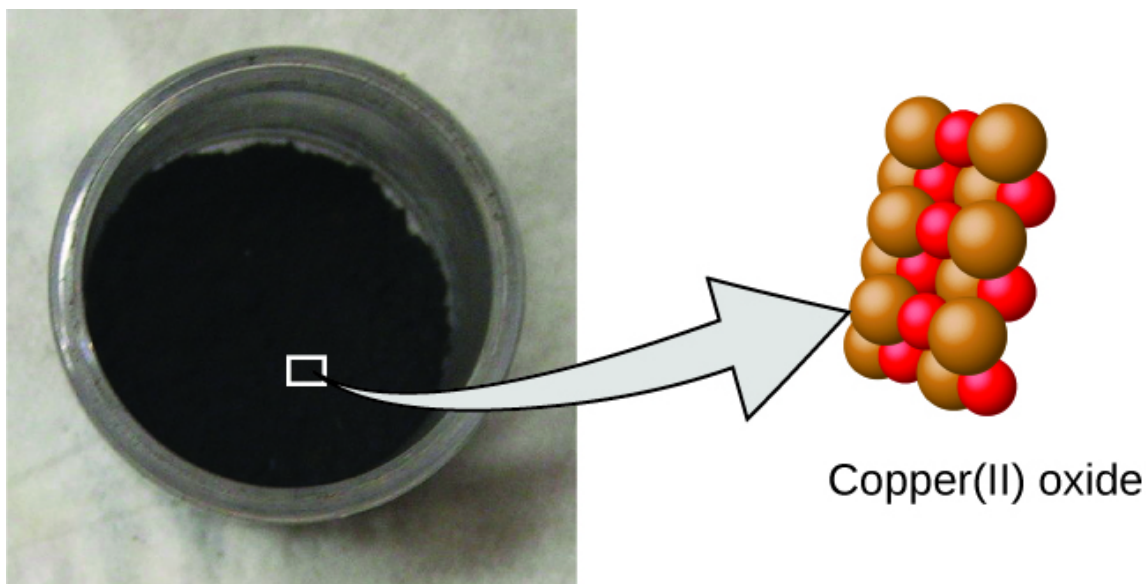
using an atomic theory. First published in 1807, many of Dalton's hypotheses about the microscopic features of matter are still valid in modern atomic theory. Here are the postulates of **Dalton's atomic theory**.

1. Matter is composed of exceedingly small particles called atoms. An atom is the smallest unit of an element that can participate in a chemical change.
2. An element consists of only one type of atom, which has a mass that is characteristic of the element and is the same for all atoms of that element ([\[link\]](#)). A macroscopic sample of an element contains an incredibly large number of atoms, all of which have identical chemical properties.



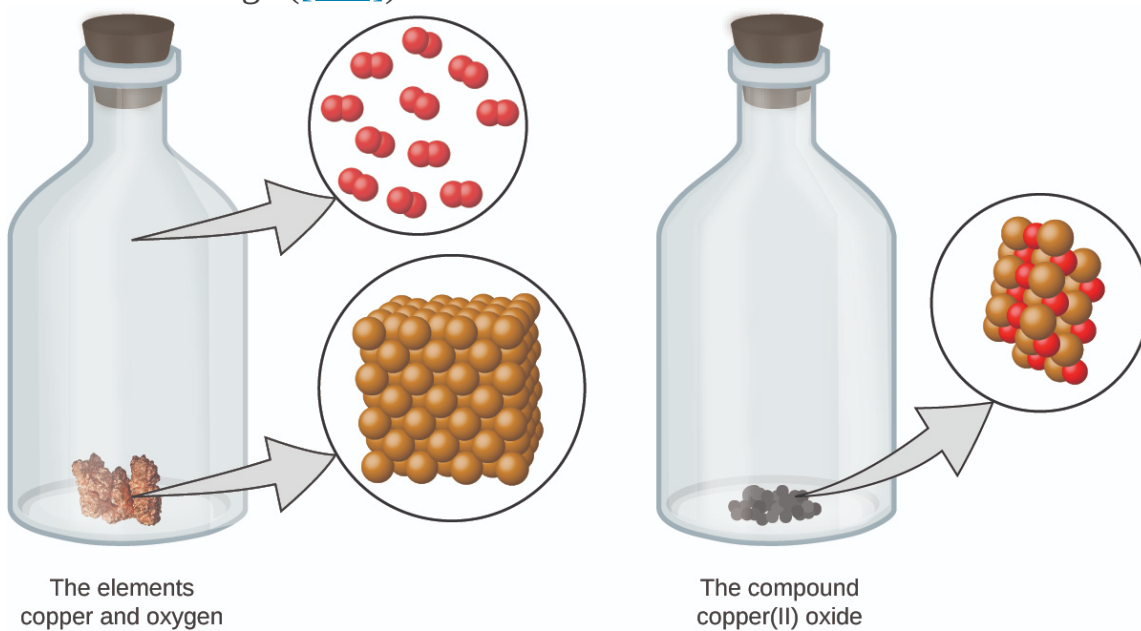
A pre-1982 copper penny (left) contains approximately 3×10^{22} copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by "slgckgc"/Flickr)

3. Atoms of one element differ in properties from atoms of all other elements.
4. A compound consists of atoms of two or more elements combined in a small, whole-number ratio. In a given compound, the numbers of atoms of each of its elements are always present in the same ratio ([\[link\]](#)).



Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (credit: modification of work by “Chemicalinterest”/Wikimedia Commons)

5. Atoms are neither created nor destroyed during a chemical change, but are instead rearranged to yield substances that are different from those present before the change ([link](#)).



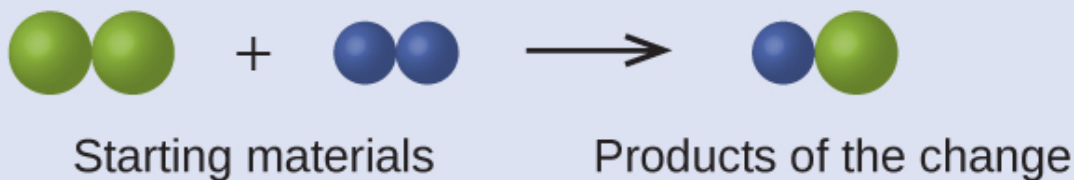
When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work by <http://images-of-elements.com/copper.php>)

Dalton's atomic theory provides a microscopic explanation of the many macroscopic properties of matter that you've learned about. For example, if an element such as copper consists of only one kind of atom, then it cannot be broken down into simpler substances, that is, into substances composed of fewer types of atoms. And if atoms are neither created nor destroyed during a chemical change, then the total mass of matter present when matter changes from one type to another will remain constant (the law of conservation of matter).

Example:

Testing Dalton's Atomic Theory

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one?

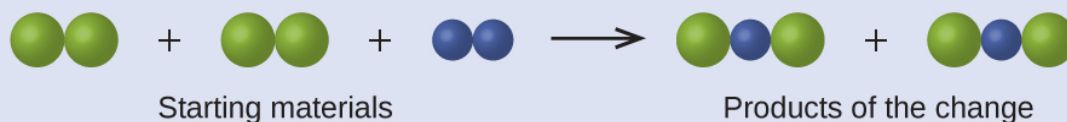


Solution

The starting materials consist of two green spheres and two purple spheres. The products consist of only one green sphere and one purple sphere. This violates Dalton's postulate that atoms are neither created nor destroyed during a chemical change, but are merely redistributed. (In this case, atoms appear to have been destroyed.)

Check Your Learning

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one?



Note:

Answer:

The starting materials consist of four green spheres and two purple spheres. The products consist of four green spheres and two purple spheres. This does not violate any of Dalton's postulates: Atoms are neither created nor destroyed, but are redistributed in small, whole-number ratios.

Dalton knew of the experiments of French chemist Joseph Proust, who demonstrated that *all samples of a pure compound contain the same elements in the same proportion by mass*. This statement is known as the **law of definite proportions** or the **law of constant composition**. The suggestion that the numbers of atoms of the elements in a given compound always exist in the same ratio is consistent with these observations. For example, when different samples of isooctane (a component of gasoline and one of the standards used in the octane rating system) are analyzed, they are found to have a carbon-to-hydrogen mass ratio of 5.33:1, as shown in [\[link\]](#).

Constant Composition of Isooctane			
Sample	Carbon	Hydrogen	Mass Ratio
A	14.82 g	2.78 g	$\frac{14.82 \text{ g carbon}}{2.78 \text{ g hydrogen}} = \frac{5.33 \text{ g carbon}}{1.00 \text{ g hydrogen}}$
B	22.33 g	4.19 g	$\frac{22.33 \text{ g carbon}}{4.19 \text{ g hydrogen}} = \frac{5.33 \text{ g carbon}}{1.00 \text{ g hydrogen}}$
C	19.40 g	3.64 g	$\frac{19.40 \text{ g carbon}}{3.63 \text{ g hydrogen}} = \frac{5.33 \text{ g carbon}}{1.00 \text{ g hydrogen}}$

It is worth noting that although all samples of a particular compound have the same mass ratio, the converse is not true in general. That is, samples that have the same mass ratio are not necessarily the same substance. For example, there are many compounds other than isooctane that also have a carbon-to-hydrogen mass ratio of 5.33:1.00.

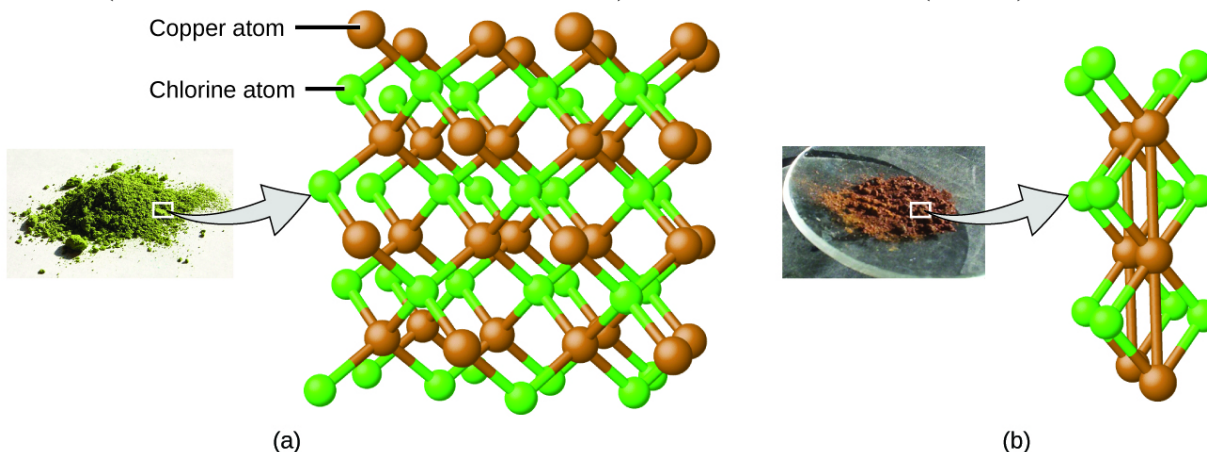
Dalton also used data from Proust, as well as results from his own experiments, to formulate another interesting law. The **law of multiple proportions** states that *when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small, whole numbers*. For example, copper and chlorine can form a green, crystalline solid with a mass ratio of 0.558 g chlorine to 1 g copper, as well as a brown crystalline solid with a mass ratio of 1.116 g chlorine to 1 g copper. These ratios by themselves may not seem particularly interesting or informative; however, if we take a ratio of these ratios, we obtain a useful and possibly surprising result: a small, whole-number ratio.

Equation:

$$\frac{\frac{1.116 \text{ g Cl}}{1 \text{ g Cu}}}{\frac{0.558 \text{ g Cl}}{1 \text{ g Cu}}} = \frac{2}{1}$$

This 2-to-1 ratio means that the brown compound has twice the amount of chlorine per amount of copper as the green compound.

This can be explained by atomic theory if the copper-to-chlorine ratio in the brown compound is 1 copper atom to 2 chlorine atoms, and the ratio in the green compound is 1 copper atom to 1 chlorine atom. The ratio of chlorine atoms (and thus the ratio of their masses) is therefore 2 to 1 ([link](#)).



Compared to the copper chlorine compound in (a), where copper is represented by brown spheres and chlorine by green spheres, the copper chlorine compound in (b) has twice as many chlorine atoms per copper atom. (credit a: modification of work by “Benjah-bmm27”/Wikimedia Commons; credit b: modification of work by “Walkerma”/Wikimedia Commons)

Example:

Laws of Definite and Multiple Proportions

A sample of compound A (a clear, colorless gas) is analyzed and found to contain 4.27 g carbon and 5.69 g oxygen. A sample of compound B (also a clear, colorless gas) is analyzed and found to contain 5.19 g carbon and 13.84 g oxygen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances A and B?

Solution

In compound A, the mass ratio of carbon to oxygen is:

Equation:

$$\frac{1.33 \text{ g O}}{1 \text{ g C}}$$

In compound B, the mass ratio of carbon to oxygen is:

Equation:

$$\frac{2.67 \text{ g O}}{1 \text{ g C}}$$

The ratio of these ratios is:

Equation:

$$\frac{\frac{1.33 \text{ g O}}{1 \text{ g C}}}{\frac{2.67 \text{ g O}}{1 \text{ g C}}} = \frac{1}{2}$$

This supports the law of multiple proportions. This means that A and B are different compounds, with A having one-half as much oxygen per amount of carbon (or twice as much carbon per amount of oxygen) as B. A possible pair of compounds that would fit this relationship would be A = CO and B = CO₂.

Check Your Learning

A sample of compound X (a clear, colorless, combustible liquid with a noticeable odor) is analyzed and found to contain 14.13 g carbon and 2.96 g hydrogen. A sample of compound Y (a clear, colorless, combustible liquid with a noticeable odor that is slightly different from X's odor) is analyzed and found to contain 19.91 g carbon and 3.34 g hydrogen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances X and Y?

Note:

Answer:

In compound X, the mass ratio of carbon to hydrogen is $\frac{14.13 \text{ g C}}{2.96 \text{ g H}}$. In compound Y, the mass ratio of carbon to oxygen is $\frac{19.91 \text{ g C}}{3.34 \text{ g H}}$. The ratio of these ratios is $\frac{\frac{14.13 \text{ g C}}{2.96 \text{ g H}}}{\frac{19.91 \text{ g C}}{3.34 \text{ g H}}} = \frac{4.77 \text{ g C/g H}}{5.96 \text{ g C/g H}} = 0.800 = \frac{4}{5}$. This small, whole-

number ratio supports the law of multiple proportions. This means that X and Y are different compounds.

Key Concepts and Summary

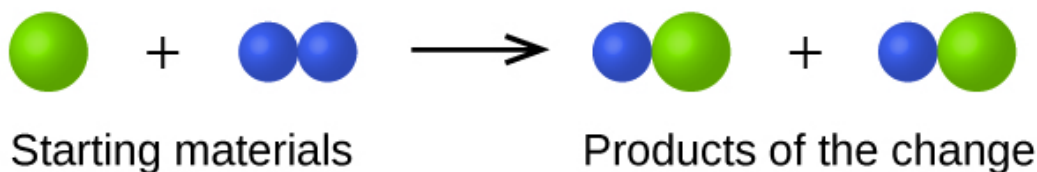
The ancient Greeks proposed that matter consists of extremely small particles called atoms. Dalton postulated that each element has a characteristic type of atom that differs in properties from atoms of all other elements, and that atoms of different elements can combine in fixed, small, whole-number ratios to form compounds. Samples of a particular compound all have the same elemental proportions by mass. When two elements form different compounds, a given mass of one element will combine with masses of the other element in a small, whole-number ratio. During any chemical change, atoms are neither created nor destroyed.

Chemistry End of Chapter Exercises

Exercise:

Problem:

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres of different elements touch, they are part of a single unit of a compound. The following chemical change represented by these spheres may violate one of the ideas of Dalton's atomic theory. Which one?



Solution:

The starting materials consist of one green sphere and two purple spheres. The products consist of two green spheres and two purple spheres. This violates Dalton's postulate that atoms are not created during a chemical change, but are merely redistributed.

Exercise:

Problem:

Which postulate of Dalton's theory is consistent with the following observation concerning the weights of reactants and products? When 100 grams of solid calcium carbonate is heated, 44 grams of carbon dioxide and 56 grams of calcium oxide are produced.

Exercise:

Problem:

Identify the postulate of Dalton's theory that is violated by the following observations: 59.95% of one sample of titanium dioxide is titanium; 60.10% of a different sample of titanium dioxide is titanium.

Solution:

This statement violates Dalton's fourth postulate: In a given compound, the numbers of atoms of each type (and thus also the percentage) always have the same ratio.

Exercise:

Problem:

Samples of compound X, Y, and Z are analyzed, with results shown here.

Compound	Description	Mass of Carbon	Mass of Hydrogen
----------	-------------	----------------	------------------

Compound	Description	Mass of Carbon	Mass of Hydrogen
X	clear, colorless, liquid with strong odor	1.776 g	0.148 g
Y	clear, colorless, liquid with strong odor	1.974 g	0.329 g
Z	clear, colorless, liquid with strong odor	7.812 g	0.651 g

Do these data provide example(s) of the law of definite proportions, the law of multiple proportions, neither, or both? What do these data tell you about compounds X, Y, and Z?

Glossary

Dalton's atomic theory

set of postulates that established the fundamental properties of atoms

law of constant composition

(also, law of definite proportions) all samples of a pure compound contain the same elements in the same proportions by mass

law of definite proportions

(also, law of constant composition) all samples of a pure compound contain the same elements in the same proportions by mass

law of multiple proportions

when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small whole numbers

Evolution of Atomic Theory

By the end of this section, you will be able to:

- Outline milestones in the development of modern atomic theory
- Summarize and interpret the results of the experiments of Thomson, Millikan, and Rutherford
- Describe the three subatomic particles that compose atoms
- Define isotopes and give examples for several elements

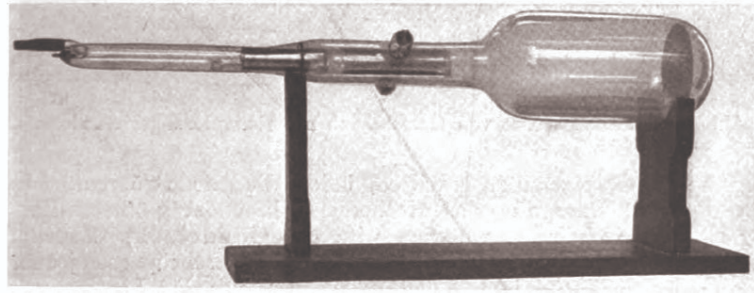
In the two centuries since Dalton developed his ideas, scientists have made significant progress in furthering our understanding of atomic theory. Much of this came from the results of several seminal experiments that revealed the details of the internal structure of atoms. Here, we will discuss some of those key developments, with an emphasis on application of the scientific method, as well as understanding how the experimental evidence was analyzed. While the historical persons and dates behind these experiments can be quite interesting, it is most important to understand the concepts resulting from their work.

Atomic Theory after the Nineteenth Century

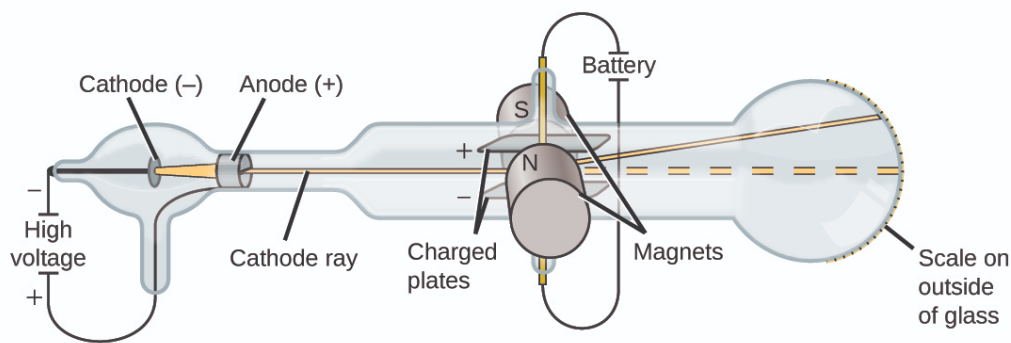
If matter were composed of atoms, what were atoms composed of? Were they the smallest particles, or was there something smaller? In the late 1800s, a number of scientists interested in questions like these investigated the electrical discharges that could be produced in low-pressure gases, with the most significant discovery made by English physicist J. J. Thomson using a cathode ray tube. This apparatus consisted of a sealed glass tube from which almost all the air had been removed; the tube contained two metal electrodes. When high voltage was applied across the electrodes, a visible beam called a cathode ray appeared between them. This beam was deflected toward the positive charge and away from the negative charge, and was produced in the same way with identical properties when different metals were used for the electrodes. In similar experiments, the ray was simultaneously deflected by an applied magnetic field, and measurements of the extent of deflection and the magnetic field strength allowed Thomson to calculate the charge-to-mass ratio of the cathode ray particles. The results of these measurements indicated that these particles were much lighter than atoms ([link](#)).



(a)



(b)



(c)

(a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end of the tube. Simultaneous deflections by applied electric and magnetic fields permitted Thomson to calculate the mass-to-charge ratio of the particles composing the cathode ray. (credit a: modification of work by Nobel Foundation; credit b: modification of work by Eugen Nesper; credit c: modification of work by “Kurzon”/Wikimedia Commons)

Based on his observations, here is what Thomson proposed and why: The particles are attracted by positive (+) charges and repelled by negative (–) charges, so they must be negatively charged (like charges repel and unlike charges attract); they are less massive than atoms and indistinguishable, regardless of the source material, so they must be fundamental, subatomic constituents of all atoms. Although controversial at the time, Thomson’s idea was gradually accepted, and his cathode ray particle is what we now call an **electron**, a negatively charged, subatomic

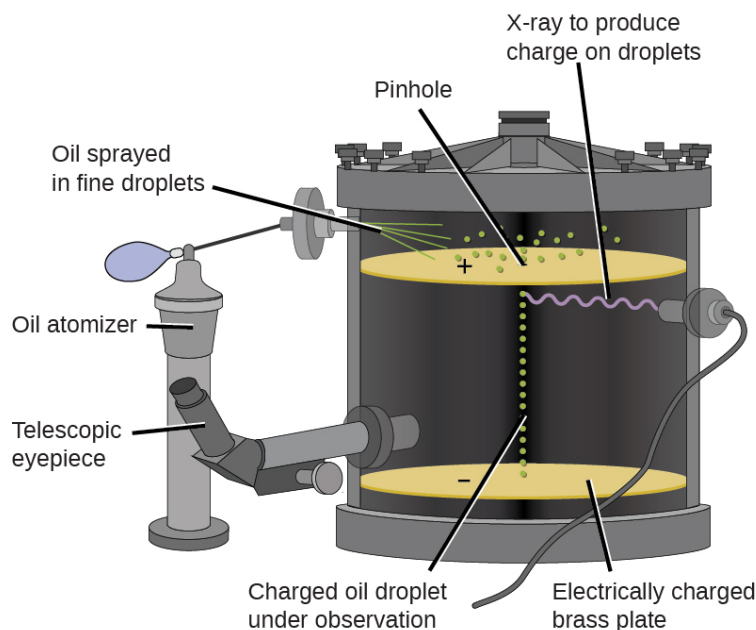
particle with a mass more than one thousand-times less that of an atom. The term “electron” was coined in 1891 by Irish physicist George Stoney, from “*electric ion.*”

Note:



Click [here](#) to hear Thomson describe his discovery in his own voice.

In 1909, more information about the electron was uncovered by American physicist Robert A. Millikan via his “oil drop” experiments. Millikan created microscopic oil droplets, which could be electrically charged by friction as they formed or by using X-rays. These droplets initially fell due to gravity, but their downward progress could be slowed or even reversed by an electric field lower in the apparatus. By adjusting the electric field strength and making careful measurements and appropriate calculations, Millikan was able to determine the charge on individual drops ([\[link\]](#)).



Oil drop	Charge in coulombs (C)
A	$4.8 \times 10^{-19} \text{ C}$
B	$3.2 \times 10^{-19} \text{ C}$
C	$6.4 \times 10^{-19} \text{ C}$
D	$1.6 \times 10^{-19} \text{ C}$
E	$4.8 \times 10^{-19} \text{ C}$

Millikan's experiment measured the charge of individual oil drops. The tabulated data are examples of a few possible values.

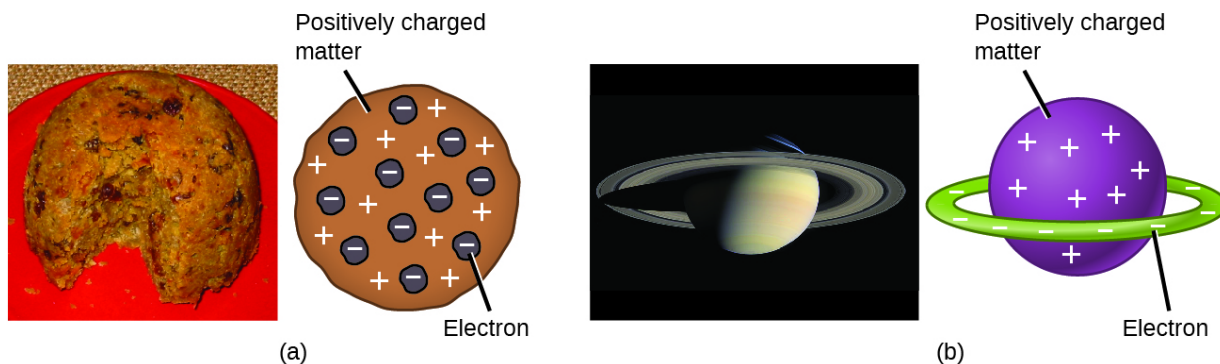
Looking at the charge data that Millikan gathered, you may have recognized that the charge of an oil droplet is always a multiple of a specific charge, $1.6 \times 10^{-19} \text{ C}$. Millikan concluded that this value must therefore be a fundamental charge—the charge of a single electron—with his measured charges due to an excess of one electron (1 times $1.6 \times 10^{-19} \text{ C}$), two electrons (2 times $1.6 \times 10^{-19} \text{ C}$), three electrons (3 times $1.6 \times 10^{-19} \text{ C}$), and so on, on a given oil droplet. Since the charge of an electron was now known due to Millikan's research, and the charge-to-mass ratio was already known due to Thomson's research ($1.759 \times 10^{11} \text{ C/kg}$), it only required a simple calculation to determine the mass of the electron as well.

Equation:

$$\text{Mass of electron} = 1.602 \times 10^{-19} \text{ C} \times \frac{1 \text{ kg}}{1.759 \times 10^{11} \text{ C}} = 9.107 \times 10^{-31} \text{ kg}$$

Scientists had now established that the atom was not indivisible as Dalton had believed, and due to the work of Thomson, Millikan, and others, the charge and mass of the negative, subatomic particles—the electrons—were known. However, the positively charged part of an atom was not yet well understood. In 1904, Thomson proposed the “plum pudding” model of atoms, which described a positively charged

mass with an equal amount of negative charge in the form of electrons embedded in it, since all atoms are electrically neutral. A competing model had been proposed in 1903 by Hantaro Nagaoka, who postulated a Saturn-like atom, consisting of a positively charged sphere surrounded by a halo of electrons ([link](#)).



- (a) Thomson suggested that atoms resembled plum pudding, an English dessert consisting of moist cake with embedded raisins (“plums”). (b) Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive “planet.” (credit a: modification of work by “Man vyi”/Wikimedia Commons; credit b: modification of work by “NASA”/Wikimedia Commons)

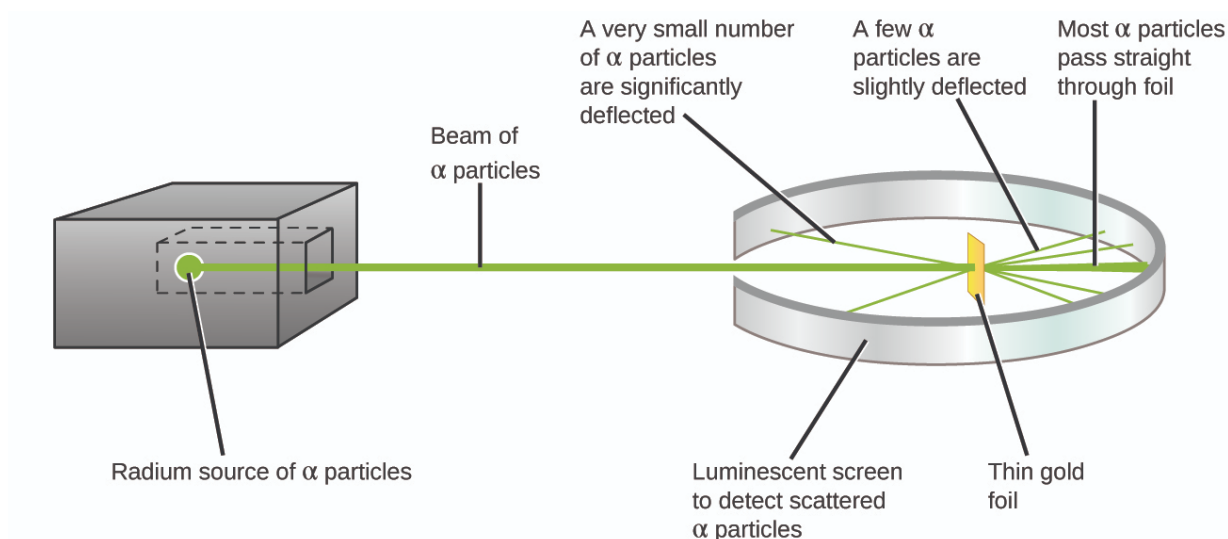
The next major development in understanding the atom came from Ernest Rutherford, a physicist from New Zealand who largely spent his scientific career in Canada and England. He performed a series of experiments using a beam of high-speed, positively charged **alpha particles (α particles)** that were produced by the radioactive decay of radium; α particles consist of two protons and two neutrons (you will learn more about radioactive decay in the chapter on nuclear chemistry). Rutherford and his colleagues Hans Geiger (later famous for the Geiger counter) and Ernest Marsden aimed a beam of α particles, the source of which was embedded in a lead block to absorb most of the radiation, at a very thin piece of gold foil and examined the resultant scattering of the α particles using a luminescent screen that glowed briefly where hit by an α particle.

What did they discover? Most particles passed right through the foil without being deflected at all. However, some were diverted slightly, and a very small number were deflected almost straight back toward the source ([link](#)). Rutherford described finding these results: “It was quite the most incredible event that has ever happened

to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you”[\[footnote\]](#) (p. 68).

Ernest Rutherford, “The Development of the Theory of Atomic Structure,” ed. J. A. Ratcliffe, in *Background to Modern Science*, eds. Joseph Needham and Walter Pagel, (Cambridge, UK: Cambridge University Press, 1938), 61–74. Accessed September 22, 2014,

<https://ia600508.us.archive.org/3/items/backgroundtomode032734mbp/backgroundtomode032734mbp.pdf>.



Geiger and Rutherford fired α particles at a piece of gold foil and detected where those particles went, as shown in this schematic diagram of their experiment. Most of the particles passed straight through the foil, but a few were deflected slightly and a very small number were significantly deflected.

Here is what Rutherford deduced: Because most of the fast-moving α particles passed through the gold atoms undeflected, they must have traveled through essentially empty space inside the atom. Alpha particles are positively charged, so deflections arose when they encountered another positive charge (like charges repel each other). Since like charges repel one another, the few positively charged α particles that changed paths abruptly must have hit, or closely approached, another body that also had a highly concentrated, positive charge. Since the deflections occurred a small fraction of the time, this charge only occupied a small amount of the space in the gold foil. Analyzing a series of such experiments in detail, Rutherford drew two conclusions:

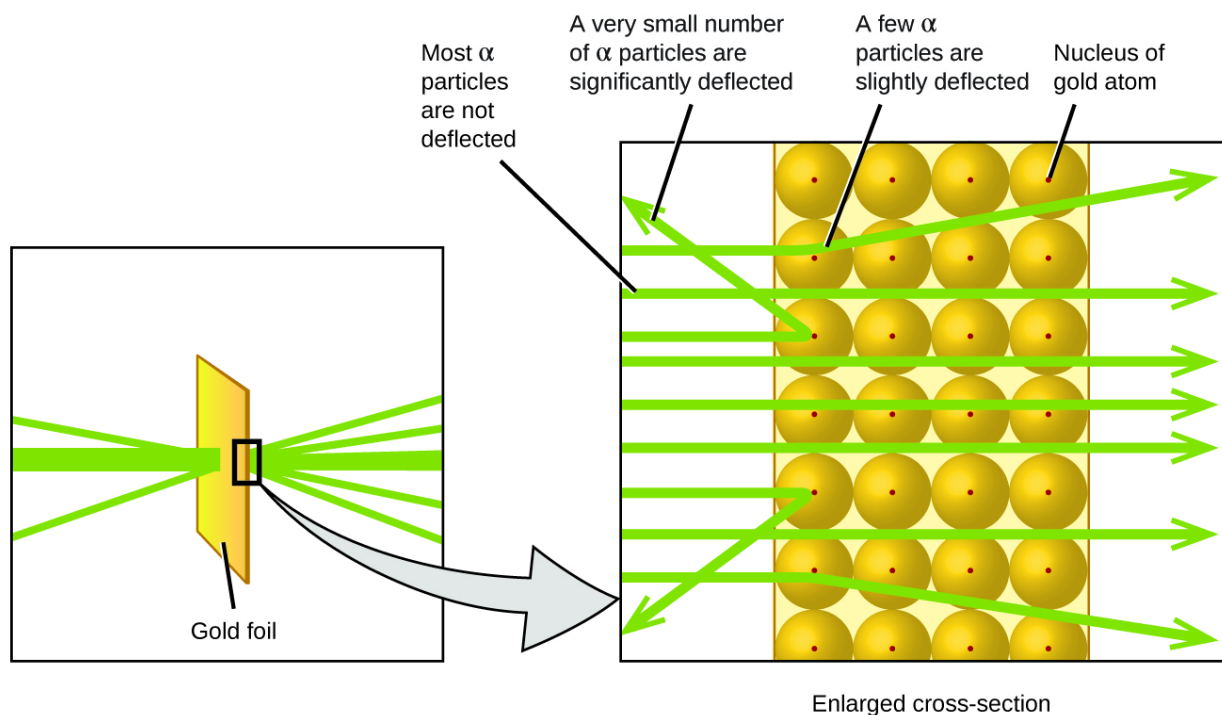
1. The volume occupied by an atom must consist of a large amount of empty space.
2. A small, relatively heavy, positively charged body, the **nucleus**, must be at the center of each atom.

Note:



View this [simulation](#) of the Rutherford gold foil experiment. Adjust the slit width to produce a narrower or broader beam of α particles to see how that affects the scattering pattern.

This analysis led Rutherford to propose a model in which an atom consists of a very small, positively charged nucleus, in which most of the mass of the atom is concentrated, surrounded by the negatively charged electrons, so that the atom is electrically neutral ([link](#)). After many more experiments, Rutherford also discovered that the nuclei of other elements contain the hydrogen nucleus as a “building block,” and he named this more fundamental particle the **proton**, the positively charged, subatomic particle found in the nucleus. With one addition, which you will learn next, this nuclear model of the atom, proposed over a century ago, is still used today.



The α particles are deflected only when they collide with or pass close to the much heavier, positively charged gold nucleus. Because the nucleus is very small compared to the size of an atom, very few α particles are deflected. Most pass through the relatively large region occupied by electrons, which are too light to deflect the rapidly moving particles.

Note:



The [Rutherford Scattering simulation](#) allows you to investigate the differences between a “plum pudding” atom and a Rutherford atom by firing α particles at each type of atom.

Another important finding was the discovery of isotopes. During the early 1900s, scientists identified several substances that appeared to be new elements, isolating them from radioactive ores. For example, a “new element” produced by the radioactive decay of thorium was initially given the name mesothorium. However, a more detailed analysis showed that mesothorium was chemically identical to radium (another decay product), despite having a different atomic mass. This result, along with similar findings for other elements, led the English chemist Frederick Soddy to realize that an element could have types of atoms with different masses that were chemically indistinguishable. These different types are called **isotopes**—atoms of the same element that differ in mass. Soddy was awarded the Nobel Prize in Chemistry in 1921 for this discovery.

One puzzle remained: The nucleus was known to contain almost all of the mass of an atom, with the number of protons only providing half, or less, of that mass. Different proposals were made to explain what constituted the remaining mass, including the existence of neutral particles in the nucleus. As you might expect, detecting uncharged particles is very challenging, and it was not until 1932 that James Chadwick found evidence of **neutrons**, uncharged, subatomic particles with a mass approximately the same as that of protons. The existence of the neutron also explained isotopes: They differ in mass because they have different numbers of neutrons, but they are chemically identical because they have the same number of protons. This will be explained in more detail later in this chapter.

Key Concepts and Summary

Although no one has actually seen the inside of an atom, experiments have demonstrated much about atomic structure. Thomson’s cathode ray tube showed that atoms contain small, negatively charged particles called electrons. Millikan discovered that there is a fundamental electric charge—the charge of an electron. Rutherford’s gold foil experiment showed that atoms have a small, dense, positively charged nucleus; the positively charged particles within the nucleus are called protons. Chadwick discovered that the nucleus also contains neutral particles called neutrons. Soddy demonstrated that atoms of the same element can differ in mass; these are called isotopes.

Chemistry End of Chapter Exercises

Exercise:

Problem:

The existence of isotopes violates one of the original ideas of Dalton's atomic theory. Which one?

Solution:

Dalton originally thought that all atoms of a particular element had identical properties, including mass. Thus, the concept of isotopes, in which an element has different masses, was a violation of the original idea. To account for the existence of isotopes, the second postulate of his atomic theory was modified to state that atoms of the same element must have identical chemical properties.

Exercise:

Problem: How are electrons and protons similar? How are they different?

Exercise:

Problem: How are protons and neutrons similar? How are they different?

Solution:

Both are subatomic particles that reside in an atom's nucleus. Both have approximately the same mass. Protons are positively charged, whereas neutrons are uncharged.

Exercise:**Problem:**

Predict and test the behavior of α particles fired at a "plum pudding" model atom.

(a) Predict the paths taken by α particles that are fired at atoms with a Thomson's plum pudding model structure. Explain why you expect the α particles to take these paths.

(b) If α particles of higher energy than those in (a) are fired at plum pudding atoms, predict how their paths will differ from the lower-energy α particle paths. Explain your reasoning.

(c) Now test your predictions from (a) and (b). Open the [Rutherford Scattering simulation](#) and select the "Plum Pudding Atom" tab. Set "Alpha Particles

Energy” to “min,” and select “show traces.” Click on the gun to start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Hit the pause button, or “Reset All.” Set “Alpha Particles Energy” to “max,” and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual paths as shown in the simulation.

Exercise:

Problem:

Predict and test the behavior of α particles fired at a Rutherford atom model.

(a) Predict the paths taken by α particles that are fired at atoms with a Rutherford atom model structure. Explain why you expect the α particles to take these paths.

(b) If α particles of higher energy than those in (a) are fired at Rutherford atoms, predict how their paths will differ from the lower-energy α particle paths. Explain your reasoning.

(c) Predict how the paths taken by the α particles will differ if they are fired at Rutherford atoms of elements other than gold. What factor do you expect to cause this difference in paths, and why?

(d) Now test your predictions from (a), (b), and (c). Open the [Rutherford Scattering simulation](#) and select the “Rutherford Atom” tab. Due to the scale of the simulation, it is best to start with a small nucleus, so select “20” for both protons and neutrons, “min” for energy, show traces, and then start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Pause or reset, set energy to “max,” and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual path as shown in the simulation. Pause or reset, select “40” for both protons and neutrons, “min” for energy, show traces, and fire away. Does this match your prediction from (c)? If not, explain why the actual path would be that shown in the simulation. Repeat this with larger numbers of protons and neutrons. What generalization can you make regarding the type of atom and effect on the path of α particles? Be clear and specific.

Solution:

(a) The Rutherford atom has a small, positively charged nucleus, so most α particles will pass through empty space far from the nucleus and be undeflected. Those α particles that pass near the nucleus will be deflected from their paths due to positive-positive repulsion. The more directly toward the nucleus the α particles are headed, the larger the deflection angle will be. (b) Higher-energy α particles that pass near the nucleus will still undergo deflection, but the faster they travel, the less the expected angle of deflection. (c) If the nucleus is smaller, the positive charge is smaller and the expected deflections are smaller—both in terms of how closely the α particles pass by the nucleus undeflected and the angle of deflection. If the nucleus is larger, the positive charge is larger and the expected deflections are larger—more α particles will be deflected, and the deflection angles will be larger. (d) The paths followed by the α particles match the predictions from (a), (b), and (c).

Glossary

alpha particle (α particle)

positively charged particle consisting of two protons and two neutrons

electron

negatively charged, subatomic particle of relatively low mass located outside the nucleus

isotopes

atoms that contain the same number of protons but different numbers of neutrons

neutron

uncharged, subatomic particle located in the nucleus

nucleus

massive, positively charged center of an atom made up of protons and neutrons

proton

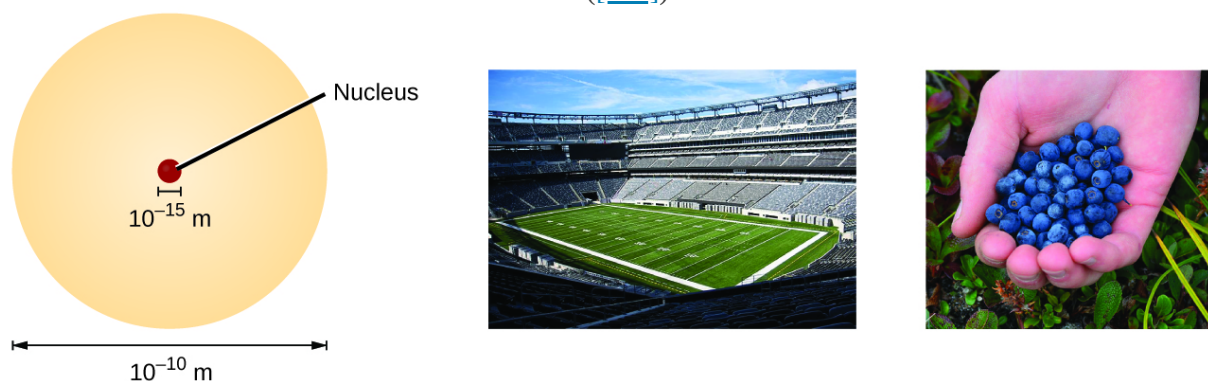
positively charged, subatomic particle located in the nucleus

Atomic Structure and Symbolism

By the end of this section, you will be able to:

- Write and interpret symbols that depict the atomic number, mass number, and charge of an atom or ion
- Define the atomic mass unit and average atomic mass
- Calculate average atomic mass and isotopic abundance

The development of modern atomic theory revealed much about the inner structure of atoms. It was learned that an atom contains a very small nucleus composed of positively charged protons and uncharged neutrons, surrounded by a much larger volume of space containing negatively charged electrons. The nucleus contains the majority of an atom's mass because protons and neutrons are much heavier than electrons, whereas electrons occupy almost all of an atom's volume. The diameter of an atom is on the order of 10^{-10} m, whereas the diameter of the nucleus is roughly 10^{-15} m—about 100,000 times smaller. For a perspective about their relative sizes, consider this: If the nucleus were the size of a blueberry, the atom would be about the size of a football stadium ([link](#)).



If an atom could be expanded to the size of a football stadium, the nucleus would be the size of a single blueberry. (credit middle: modification of work by “babyknight”/Wikimedia Commons; credit right: modification of work by Paxson Woelber)

Atoms—and the protons, neutrons, and electrons that compose them—are extremely small. For example, a carbon atom weighs less than 2×10^{-23} g, and an electron has a charge of less than 2×10^{-19} C (coulomb). When describing the properties of tiny objects such as atoms, we use appropriately small units of measure, such as the **atomic mass unit (amu)** and the **fundamental unit of charge (e)**. The amu was originally defined based on hydrogen, the lightest element, then later in terms of oxygen. Since 1961, it has been defined with regard to the most abundant isotope of carbon, atoms of which are assigned masses of exactly 12 amu. (This isotope is known as “carbon-12” as will be discussed later in this module.) Thus, one amu is exactly $\frac{1}{12}$ of the mass of one carbon-12 atom: $1 \text{ amu} = 1.6605 \times 10^{-24}$ g. (The **Dalton (Da)** and the **unified atomic mass unit (u)** are alternative units that are equivalent to the amu.) The fundamental unit of charge (also called the elementary charge) equals the magnitude of the charge of an electron (e) with $e = 1.602 \times 10^{-19}$ C.

A proton has a mass of 1.0073 amu and a charge of 1+. A neutron is a slightly heavier particle with a mass 1.0087 amu and a charge of zero; as its name suggests, it is neutral. The electron has a charge of 1– and is a much lighter particle with a mass of about 0.00055 amu (it would take about 1800 electrons to equal the mass of one proton). The properties of these fundamental particles are summarized in [link](#). (An observant student might notice that the sum of an atom's subatomic particles does not equal the atom's actual mass: The total mass of six protons, six neutrons, and six electrons is 12.0993 amu, slightly larger than 12.00

amu. This “missing” mass is known as the mass defect, and you will learn about it in the chapter on nuclear chemistry.)

Properties of Subatomic Particles					
Name	Location	Charge (C)	Unit Charge	Mass (amu)	Mass (g)
electron	outside nucleus	-1.602×10^{-19}	1 [−]	0.00055	0.00091×10^{-24}
proton	nucleus	1.602×10^{-19}	1 ⁺	1.00727	1.67262×10^{-24}
neutron	nucleus	0	0	1.00866	1.67493×10^{-24}

The number of protons in the nucleus of an atom is its **atomic number (Z)**. This is the defining trait of an element: Its value determines the identity of the atom. For example, any atom that contains six protons is the element carbon and has the atomic number 6, regardless of how many neutrons or electrons it may have. A neutral atom must contain the same number of positive and negative charges, so the number of protons equals the number of electrons. Therefore, the atomic number also indicates the number of electrons in an atom. The total number of protons and neutrons in an atom is called its **mass number (A)**. The number of neutrons is therefore the difference between the mass number and the atomic number: $A - Z$ = number of neutrons.

Equation:

$$\begin{aligned}\text{atomic number (Z)} &= \text{number of protons} \\ \text{mass number (A)} &= \text{number of protons} + \text{number of neutrons} \\ A - Z &= \text{number of neutrons}\end{aligned}$$

Atoms are electrically neutral if they contain the same number of positively charged protons and negatively charged electrons. When the numbers of these subatomic particles are *not* equal, the atom is electrically charged and is called an **ion**. The charge of an atom is defined as follows:

$$\text{Atomic charge} = \text{number of protons} - \text{number of electrons}$$

As will be discussed in more detail later in this chapter, atoms (and molecules) typically acquire charge by gaining or losing electrons. An atom that gains one or more electrons will exhibit a negative charge and is called an **anion**. Positively charged atoms called **cations** are formed when an atom loses one or more electrons. For example, a neutral sodium atom ($Z = 11$) has 11 electrons. If this atom loses one electron, it will become a cation with a 1⁺ charge ($11 - 10 = 1+$). A neutral oxygen atom ($Z = 8$) has eight electrons, and if it gains two electrons it will become an anion with a 2[−] charge ($8 - 10 = 2-$).

Example:**Composition of an Atom**

Iodine is an essential trace element in our diet; it is needed to produce thyroid hormone. Insufficient iodine in the diet can lead to the development of a goiter, an enlargement of the thyroid gland ([link](#)).



(a)



(b)

(a) Insufficient iodine in the diet can cause an enlargement of the thyroid gland called a goiter. (b) The addition of small amounts of iodine to salt, which prevents the formation of goiters, has helped eliminate this concern in the US where salt consumption is high. (credit a: modification of work by "Almazi"/Wikimedia Commons; credit b: modification of work by Mike Mozart)

The addition of small amounts of iodine to table salt (iodized salt) has essentially eliminated this health concern in the United States, but as much as 40% of the world's population is still at risk of iodine deficiency. The iodine atoms are added as anions, and each has a 1^- charge and a mass number of 127. Determine the numbers of protons, neutrons, and electrons in one of these iodine anions.

Solution

The atomic number of iodine (53) tells us that a neutral iodine atom contains 53 protons in its nucleus and 53 electrons outside its nucleus. Because the sum of the numbers of protons and neutrons equals the mass number, 127, the number of neutrons is 74 ($127 - 53 = 74$). Since the iodine is added as a 1^- anion, the number of electrons is 54 [$53 - (1^-) = 54$].

Check Your Learning

An ion of platinum has a mass number of 195 and contains 74 electrons. How many protons and neutrons does it contain, and what is its charge?

Note:**Answer:**

78 protons; 117 neutrons; charge is $4+$

Chemical Symbols

A **chemical symbol** is an abbreviation that we use to indicate an element or an atom of an element. For example, the symbol for mercury is Hg ([link](#)). We use the same symbol to indicate one atom of mercury (microscopic domain) or to label a container of many atoms of the element mercury (macroscopic domain).



The symbol Hg represents the element mercury regardless of the amount; it could represent one atom of mercury or a large amount of mercury.

The symbols for several common elements and their atoms are listed in [link](#). Some symbols are derived from the common name of the element; others are abbreviations of the name in another language. Most symbols have one or two letters, but three-letter symbols have been used to describe some elements that have atomic numbers greater than 112. To avoid confusion with other notations, only the first letter of a symbol is capitalized. For example, Co is the symbol for the element cobalt, but CO is the notation for the compound carbon monoxide, which contains atoms of the elements carbon (C) and oxygen (O). All known elements and their symbols are in the periodic table in [link](#) (also found in [link](#)).

Some Common Elements and Their Symbols			
Element	Symbol	Element	Symbol
aluminum	Al	iron	Fe (from <i>ferrum</i>)

Some Common Elements and Their Symbols			
Element	Symbol	Element	Symbol
bromine	Br	lead	Pb (from <i>plumbum</i>)
calcium	Ca	magnesium	Mg
carbon	C	mercury	Hg (from <i>hydrargyrum</i>)
chlorine	Cl	nitrogen	N
chromium	Cr	oxygen	O
cobalt	Co	potassium	K (from <i>kalium</i>)
copper	Cu (from <i>cuprum</i>)	silicon	Si
fluorine	F	silver	Ag (from <i>argentum</i>)
gold	Au (from <i>aurum</i>)	sodium	Na (from <i>natrium</i>)
helium	He	sulfur	S
hydrogen	H	tin	Sn (from <i>stannum</i>)
iodine	I	zinc	Zn

Traditionally, the discoverer (or discoverers) of a new element names the element. However, until the name is recognized by the International Union of Pure and Applied Chemistry (IUPAC), the recommended name of the new element is based on the Latin word(s) for its atomic number. For example, element 106 was called unnilhexium (Unh), element 107 was called unnilseptium (Uns), and element 108 was called unniloctium (Uno) for several years. These elements are now named after scientists (or occasionally locations); for example, element 106 is now known as *seaborgium* (Sg) in honor of Glenn Seaborg, a Nobel Prize winner who was active in the discovery of several heavy elements.

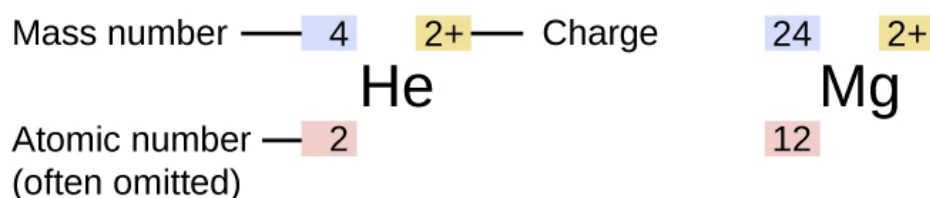
Note:



Visit this [site](#) to learn more about IUPAC, the International Union of Pure and Applied Chemistry, and explore its periodic table.

Isotopes

The symbol for a specific isotope of any element is written by placing the mass number as a superscript to the left of the element symbol ([link](#)). The atomic number is sometimes written as a subscript preceding the symbol, but since this number defines the element's identity, as does its symbol, it is often omitted. For example, magnesium exists as a mixture of three isotopes, each with an atomic number of 12 and with mass numbers of 24, 25, and 26, respectively. These isotopes can be identified as ^{24}Mg , ^{25}Mg , and ^{26}Mg . These isotope symbols are read as “element, mass number” and can be symbolized consistent with this reading. For instance, ^{24}Mg is read as “magnesium 24,” and can be written as “magnesium-24” or “Mg-24.” ^{25}Mg is read as “magnesium 25,” and can be written as “magnesium-25” or “Mg-25.” All magnesium atoms have 12 protons in their nucleus. They differ only because a ^{24}Mg atom has 12 neutrons in its nucleus, a ^{25}Mg atom has 13 neutrons, and a ^{26}Mg has 14 neutrons.



The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

Information about the naturally occurring isotopes of elements with atomic numbers 1 through 10 is given in [link](#). Note that in addition to standard names and symbols, the isotopes of hydrogen are often referred to using common names and accompanying symbols. Hydrogen-2, symbolized ^2H , is also called deuterium and sometimes symbolized D. Hydrogen-3, symbolized ^3H , is also called tritium and sometimes symbolized T.

Nuclear Compositions of Atoms of the Very Light Elements						
Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
hydrogen	^1_1H (protium)	1	1	0	1.0078	99.989
	^2_1H (deuterium)	1	1	1	2.0141	0.0115

Nuclear Compositions of Atoms of the Very Light Elements						
Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
	${}^3_1\text{H}$ (tritium)	1	1	2	3.01605	— (trace)
helium	${}^3_2\text{He}$	2	2	1	3.01603	0.00013
	${}^4_2\text{He}$	2	2	2	4.0026	100
lithium	${}^6_3\text{Li}$	3	3	3	6.0151	7.59
	${}^7_3\text{Li}$	3	3	4	7.0160	92.41
beryllium	${}^9_4\text{Be}$	4	4	5	9.0122	100
boron	${}^{10}_5\text{B}$	5	5	5	10.0129	19.9
	${}^{11}_5\text{B}$	5	5	6	11.0093	80.1
carbon	${}^{12}_6\text{C}$	6	6	6	12.0000	98.89
	${}^{13}_6\text{C}$	6	6	7	13.0034	1.11
	${}^{14}_6\text{C}$	6	6	8	14.0032	— (trace)
nitrogen	${}^{14}_7\text{N}$	7	7	7	14.0031	99.63
	${}^{15}_7\text{N}$	7	7	8	15.0001	0.37
oxygen	${}^{16}_8\text{O}$	8	8	8	15.9949	99.757
	${}^{17}_8\text{O}$	8	8	9	16.9991	0.038
	${}^{18}_8\text{O}$	8	8	10	17.9992	0.205
fluorine	${}^{19}_9\text{F}$	9	9	10	18.9984	100
neon	${}^{20}_{10}\text{Ne}$	10	10	10	19.9924	90.48
	${}^{21}_{10}\text{Ne}$	10	10	11	20.9938	0.27
	${}^{22}_{10}\text{Ne}$	10	10	12	21.9914	9.25

Note:



Use this [Build an Atom simulator](#) to build atoms of the first 10 elements, see which isotopes exist, check nuclear stability, and gain experience with isotope symbols.

Atomic Mass

Because each proton and each neutron contribute approximately one amu to the mass of an atom, and each electron contributes far less, the **atomic mass** of a single atom is approximately equal to its mass number (a whole number). However, the average masses of atoms of most elements are not whole numbers because most elements exist naturally as mixtures of two or more isotopes.

The mass of an element shown in a periodic table or listed in a table of atomic masses is a weighted, average mass of all the isotopes present in a naturally occurring sample of that element. This is equal to the sum of each individual isotope's mass multiplied by its fractional abundance.

Equation:

$$\text{average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i$$

For example, the element boron is composed of two isotopes: About 19.9% of all boron atoms are ^{10}B with a mass of 10.0129 amu, and the remaining 80.1% are ^{11}B with a mass of 11.0093 amu. The average atomic mass for boron is calculated to be:

Equation:

$$\begin{aligned}\text{boron average mass} &= (0.199 \times 10.0129 \text{ amu}) + (0.801 \times 11.0093 \text{ amu}) \\ &= 1.99 \text{ amu} + 8.82 \text{ amu} \\ &= 10.81 \text{ amu}\end{aligned}$$

It is important to understand that no single boron atom weighs exactly 10.8 amu; 10.8 amu is the average mass of all boron atoms, and individual boron atoms weigh either approximately 10 amu or 11 amu.

Example:

Calculation of Average Atomic Mass

A meteorite found in central Indiana contains traces of the noble gas neon picked up from the solar wind during the meteorite's trip through the solar system. Analysis of a sample of the gas showed that it consisted of 91.84% ^{20}Ne (mass 19.9924 amu), 0.47% ^{21}Ne (mass 20.9940 amu), and 7.69% ^{22}Ne (mass 21.9914 amu). What is the average mass of the neon in the solar wind?

Solution

Equation:

$$\begin{aligned}
 \text{average mass} &= (0.9184 \times 19.9924 \text{ amu}) + (0.0047 \times 20.9940 \text{ amu}) + (0.0769 \times 21.9914 \text{ amu}) \\
 &= (18.36 + 0.099 + 1.69) \text{ amu} \\
 &= 20.15 \text{ amu}
 \end{aligned}$$

The average mass of a neon atom in the solar wind is 20.15 amu. (The average mass of a terrestrial neon atom is 20.1796 amu. This result demonstrates that we may find slight differences in the natural abundance of isotopes, depending on their origin.)

Check Your Learning

A sample of magnesium is found to contain 78.70% of ^{24}Mg atoms (mass 23.98 amu), 10.13% of ^{25}Mg atoms (mass 24.99 amu), and 11.17% of ^{26}Mg atoms (mass 25.98 amu). Calculate the average mass of a Mg atom.

Note:

Answer:

24.31 amu

We can also do variations of this type of calculation, as shown in the next example.

Example:

Calculation of Percent Abundance

Naturally occurring chlorine consists of ^{35}Cl (mass 34.96885 amu) and ^{37}Cl (mass 36.96590 amu), with an average mass of 35.453 amu. What is the percent composition of Cl in terms of these two isotopes?

Solution

The average mass of chlorine is the fraction that is ^{35}Cl times the mass of ^{35}Cl plus the fraction that is ^{37}Cl times the mass of ^{37}Cl .

Equation:

$$\text{average mass} = (\text{fraction of } ^{35}\text{Cl} \times \text{mass of } ^{35}\text{Cl}) + (\text{fraction of } ^{37}\text{Cl} \times \text{mass of } ^{37}\text{Cl})$$

If we let x represent the fraction that is ^{35}Cl , then the fraction that is ^{37}Cl is represented by $1.00 - x$. (The fraction that is ^{35}Cl + the fraction that is ^{37}Cl must add up to 1, so the fraction of ^{37}Cl must equal $1.00 - \text{the fraction of } ^{35}\text{Cl}$.)

Substituting this into the average mass equation, we have:

Equation:

$$\begin{aligned}
 35.453 \text{ amu} &= (x \times 34.96885 \text{ amu}) + [(1.00 - x) \times 36.96590 \text{ amu}] \\
 35.453 &= 34.96885x + 36.96590 - 36.96590x \\
 1.99705x &= 1.513 \\
 x &= \frac{1.513}{1.99705} = 0.7576
 \end{aligned}$$

So solving yields: $x = 0.7576$, which means that $1.00 - 0.7576 = 0.2424$. Therefore, chlorine consists of 75.76% ^{35}Cl and 24.24% ^{37}Cl .

Check Your Learning

Naturally occurring copper consists of ^{63}Cu (mass 62.9296 amu) and ^{65}Cu (mass 64.9278 amu), with an average mass of 63.546 amu. What is the percent composition of Cu in terms of these two isotopes?

Note:

Answer:

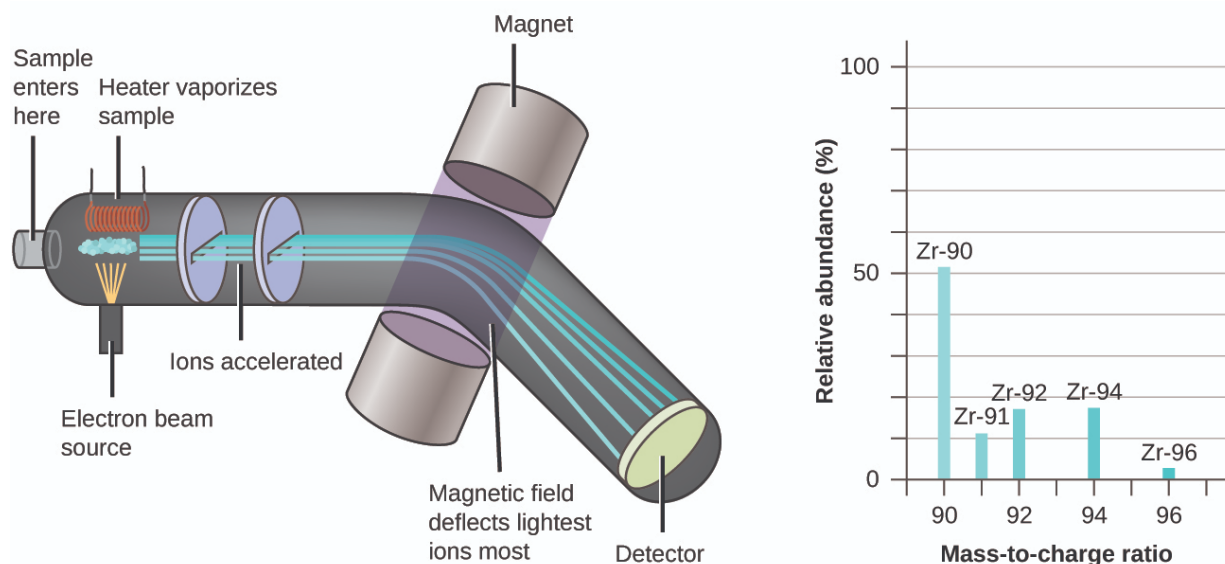
69.15% Cu-63 and 30.85% Cu-65

Note:



Visit this [site](#) to make mixtures of the main isotopes of the first 18 elements, gain experience with average atomic mass, and check naturally occurring isotope ratios using the Isotopes and Atomic Mass simulation.

The occurrence and natural abundances of isotopes can be experimentally determined using an instrument called a mass spectrometer. Mass spectrometry (MS) is widely used in chemistry, forensics, medicine, environmental science, and many other fields to analyze and help identify the substances in a sample of material. In a typical mass spectrometer ([link](#)), the sample is vaporized and exposed to a high-energy electron beam that causes the sample's atoms (or molecules) to become electrically charged, typically by losing one or more electrons. These cations then pass through a (variable) electric or magnetic field that deflects each cation's path to an extent that depends on both its mass and charge (similar to how the path of a large steel ball bearing rolling past a magnet is deflected to a lesser extent than that of a small steel BB). The ions are detected, and a plot of the relative number of ions generated versus their mass-to-charge ratios (a *mass spectrum*) is made. The height of each vertical feature or peak in a mass spectrum is proportional to the fraction of cations with the specified mass-to-charge ratio. Since its initial use during the development of modern atomic theory, MS has evolved to become a powerful tool for chemical analysis in a wide range of applications.



Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr.

Note:



See an [animation](#) that explains mass spectrometry. Watch this [video](#) from the Royal Society for Chemistry for a brief description of the rudiments of mass spectrometry.

Key Concepts and Summary

An atom consists of a small, positively charged nucleus surrounded by electrons. The nucleus contains protons and neutrons; its diameter is about 100,000 times smaller than that of the atom. The mass of one atom is usually expressed in atomic mass units (amu), which is referred to as the atomic mass. An amu is defined as exactly $\frac{1}{12}$ of the mass of a carbon-12 atom and is equal to 1.6605×10^{-24} g.

Protons are relatively heavy particles with a charge of $1+$ and a mass of 1.0073 amu. Neutrons are relatively heavy particles with no charge and a mass of 1.0087 amu. Electrons are light particles with a charge of $1-$ and a mass of 0.00055 amu. The number of protons in the nucleus is called the atomic number (Z) and is the property that defines an atom's elemental identity. The sum of the numbers of protons and neutrons in the nucleus is called the mass number and, expressed in amu, is approximately equal to the mass of the atom. An atom is neutral when it contains equal numbers of electrons and protons.

Isotopes of an element are atoms with the same atomic number but different mass numbers; isotopes of an element, therefore, differ from each other only in the number of neutrons within the nucleus. When a naturally occurring element is composed of several isotopes, the atomic mass of the element represents the average of the masses of the isotopes involved. A chemical symbol identifies the atoms in a substance using symbols, which are one-, two-, or three-letter abbreviations for the atoms.

Key Equations

- average mass = $\sum_i (\text{fractional abundance} \times \text{isotopic mass})_i$

Chemistry End of Chapter Exercises

Exercise:

Problem:

In what way are isotopes of a given element always different? In what way(s) are they always the same?

Exercise:

Problem: Write the symbol for each of the following ions:

- (a) the ion with a 1+ charge, atomic number 55, and mass number 133
- (b) the ion with 54 electrons, 53 protons, and 74 neutrons
- (c) the ion with atomic number 15, mass number 31, and a 3- charge
- (d) the ion with 24 electrons, 30 neutrons, and a 3+ charge

Solution:

(a) $^{133}\text{Cs}^+$; (b) $^{127}\text{I}^-$; (c) $^{31}\text{P}^{3-}$; (d) $^{57}\text{Co}^{3+}$

Exercise:

Problem: Write the symbol for each of the following ions:

- (a) the ion with a 3+ charge, 28 electrons, and a mass number of 71
- (b) the ion with 36 electrons, 35 protons, and 45 neutrons
- (c) the ion with 86 electrons, 142 neutrons, and a 4+ charge
- (d) the ion with a 2+ charge, atomic number 38, and mass number 87

Exercise:

Problem: Open the [Build an Atom simulation](#) and click on the Atom icon.

- (a) Pick any one of the first 10 elements that you would like to build and state its symbol.

(b) Drag protons, neutrons, and electrons onto the atom template to make an atom of your element. State the numbers of protons, neutrons, and electrons in your atom, as well as the net charge and mass number.

(c) Click on “Net Charge” and “Mass Number,” check your answers to (b), and correct, if needed.

(d) Predict whether your atom will be stable or unstable. State your reasoning.

(e) Check the “Stable/Unstable” box. Was your answer to (d) correct? If not, first predict what you can do to make a stable atom of your element, and then do it and see if it works. Explain your reasoning.

Solution:

(a) Carbon-12, ^{12}C ; (b) This atom contains six protons and six neutrons. There are six electrons in a neutral ^{12}C atom. The net charge of such a neutral atom is zero, and the mass number is 12. (c) The preceding answers are correct. (d) The atom will be stable since C-12 is a stable isotope of carbon. (e) The preceding answer is correct. Other answers for this exercise are possible if a different element of isotope is chosen.

Exercise:

Problem: Open the [Build an Atom simulation](#)

(a) Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Oxygen-16 and give the isotope symbol for this atom.

(b) Now add two more electrons to make an ion and give the symbol for the ion you have created.

Exercise:

Problem: Open the [Build an Atom simulation](#)

(a) Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Lithium-6 and give the isotope symbol for this atom.

(b) Now remove one electron to make an ion and give the symbol for the ion you have created.

Solution:

(a) Lithium-6 contains three protons, three neutrons, and three electrons. The isotope symbol is ^6Li or ^6_3Li . (b) $^6\text{Li}^+$ or $^6_3\text{Li}^+$

Exercise:

Problem:

Determine the number of protons, neutrons, and electrons in the following isotopes that are used in medical diagnoses:

(a) atomic number 9, mass number 18, charge of $1-$

(b) atomic number 43, mass number 99, charge of $7+$

(c) atomic number 53, atomic mass number 131, charge of $1-$

(d) atomic number 81, atomic mass number 201, charge of $1+$

(e) Name the elements in parts (a), (b), (c), and (d).

Exercise:

Problem:

The following are properties of isotopes of two elements that are essential in our diet. Determine the number of protons, neutrons and electrons in each and name them.

(a) atomic number 26, mass number 58, charge of 2+

(b) atomic number 53, mass number 127, charge of 1-

Solution:

(a) Iron, 26 protons, 24 electrons, and 32 neutrons; (b) iodine, 53 protons, 54 electrons, and 74 neutrons

Exercise:

Problem:

Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:

(a) $^{10}_5\text{B}$

(b) $^{199}_{80}\text{Hg}$

(c) $^{63}_{29}\text{Cu}$

(d) $^{13}_6\text{C}$

(e) $^{77}_{34}\text{Se}$

Exercise:

Problem:

Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:

(a) ^7_3Li

(b) $^{125}_{52}\text{Te}$

(c) $^{109}_{47}\text{Ag}$

(d) $^{15}_7\text{N}$

(e) $^{31}_{15}\text{P}$

Solution:

(a) 3 protons, 3 electrons, 4 neutrons; (b) 52 protons, 52 electrons, 73 neutrons; (c) 47 protons, 47 electrons, 62 neutrons; (d) 7 protons, 7 electrons, 8 neutrons; (e) 15 protons, 15 electrons, 16 neutrons

Exercise:

Problem:

Click on the [site](#) and select the “Mix Isotopes” tab, hide the “Percent Composition” and “Average Atomic Mass” boxes, and then select the element boron.

(a) Write the symbols of the isotopes of boron that are shown as naturally occurring in significant amounts.

(b) Predict the relative amounts (percentages) of these boron isotopes found in nature. Explain the reasoning behind your choice.

(c) Add isotopes to the black box to make a mixture that matches your prediction in (b). You may drag isotopes from their bins or click on “More” and then move the sliders to the appropriate amounts.

(d) Reveal the “Percent Composition” and “Average Atomic Mass” boxes. How well does your mixture match with your prediction? If necessary, adjust the isotope amounts to match your prediction.

(e) Select “Nature’s” mix of isotopes and compare it to your prediction. How well does your prediction compare with the naturally occurring mixture? Explain. If necessary, adjust your amounts to make them match “Nature’s” amounts as closely as possible.

Exercise:

Problem: Repeat [\[link\]](#) using an element that has three naturally occurring isotopes.

Solution:

Let us use neon as an example. Since there are three isotopes, there is no way to be sure to accurately predict the abundances to make the total of 20.18 amu average atomic mass. Let us guess that the abundances are 9% Ne-22, 91% Ne-20, and only a trace of Ne-21. The average mass would be 20.18 amu. Checking the nature’s mix of isotopes shows that the abundances are 90.48% Ne-20, 9.25% Ne-22, and 0.27% Ne-21, so our guessed amounts have to be slightly adjusted.

Exercise:**Problem:**

An element has the following natural abundances and isotopic masses: 90.92% abundance with 19.99 amu, 0.26% abundance with 20.99 amu, and 8.82% abundance with 21.99 amu. Calculate the average atomic mass of this element.

Exercise:**Problem:**

Average atomic masses listed by IUPAC are based on a study of experimental results. Bromine has two isotopes ^{79}Br and ^{81}Br , whose masses (78.9183 and 80.9163 amu) and abundances (50.69% and 49.31%) were determined in earlier experiments. Calculate the average atomic mass of bromine based on these experiments.

Solution:

79.904 amu

Exercise:

Problem:

Variations in average atomic mass may be observed for elements obtained from different sources. Lithium provides an example of this. The isotopic composition of lithium from naturally occurring minerals is 7.5% ${}^6\text{Li}$ and 92.5% ${}^7\text{Li}$, which have masses of 6.01512 amu and 7.01600 amu, respectively. A commercial source of lithium, recycled from a military source, was 3.75% ${}^6\text{Li}$ (and the rest ${}^7\text{Li}$). Calculate the average atomic mass values for each of these two sources.

Exercise:**Problem:**

The average atomic masses of some elements may vary, depending upon the sources of their ores. Naturally occurring boron consists of two isotopes with accurately known masses (${}^{10}\text{B}$, 10.0129 amu and ${}^{11}\text{B}$, 11.0931 amu). The actual atomic mass of boron can vary from 10.807 to 10.819, depending on whether the mineral source is from Turkey or the United States. Calculate the percent abundances leading to the two values of the average atomic masses of boron from these two countries.

Solution:

Turkey source: 26.49% (of 10.0129 amu isotope); US source: 25.37% (of 10.0129 amu isotope)

Exercise:**Problem:**

The ${}^{18}\text{O}$: ${}^{16}\text{O}$ abundance ratio in some meteorites is greater than that used to calculate the average atomic mass of oxygen on earth. Is the average mass of an oxygen atom in these meteorites greater than, less than, or equal to that of a terrestrial oxygen atom?

Glossary

anion

negatively charged atom or molecule (contains more electrons than protons)

atomic mass

average mass of atoms of an element, expressed in amu

atomic mass unit (amu)

(also, unified atomic mass unit, u, or Dalton, Da) unit of mass equal to $\frac{1}{12}$ of the mass of a ${}^{12}\text{C}$ atom

atomic number (Z)

number of protons in the nucleus of an atom

cation

positively charged atom or molecule (contains fewer electrons than protons)

chemical symbol

one-, two-, or three-letter abbreviation used to represent an element or its atoms

Dalton (Da)

alternative unit equivalent to the atomic mass unit

fundamental unit of charge

(also called the elementary charge) equals the magnitude of the charge of an electron (e) with $e = 1.602 \times 10^{-19} \text{ C}$

ion

electrically charged atom or molecule (contains unequal numbers of protons and electrons)

mass number (A)

sum of the numbers of neutrons and protons in the nucleus of an atom

unified atomic mass unit (u)

alternative unit equivalent to the atomic mass unit

Chemical Formulas

By the end of this section, you will be able to:

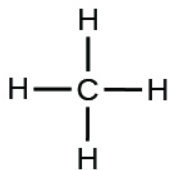
- Symbolize the composition of molecules using molecular formulas and empirical formulas
- Represent the bonding arrangement of atoms within molecules using structural formulas

A **molecular formula** is a representation of a molecule that uses chemical symbols to indicate the types of atoms followed by subscripts to show the number of atoms of each type in the molecule. (A subscript is used only when more than one atom of a given type is present.) Molecular formulas are also used as abbreviations for the names of compounds.

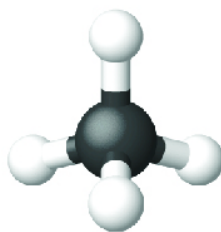
The **structural formula** for a compound gives the same information as its molecular formula (the types and numbers of atoms in the molecule) but also shows how the atoms are connected in the molecule. The structural formula for methane contains symbols for one C atom and four H atoms, indicating the number of atoms in the molecule ([\[link\]](#)). The lines represent bonds that hold the atoms together. (A chemical bond is an attraction between atoms or ions that holds them together in a molecule or a crystal.) We will discuss chemical bonds and see how to predict the arrangement of atoms in a molecule later. For now, simply know that the lines are an indication of how the atoms are connected in a molecule. A ball-and-stick model shows the geometric arrangement of the atoms with atomic sizes not to scale, and a space-filling model shows the relative sizes of the atoms.



(a)



(b)



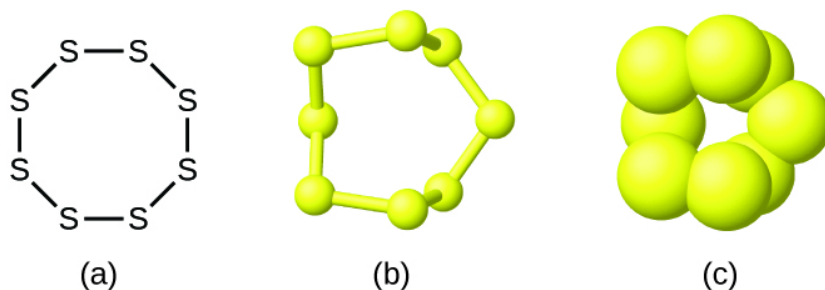
(c)



(d)

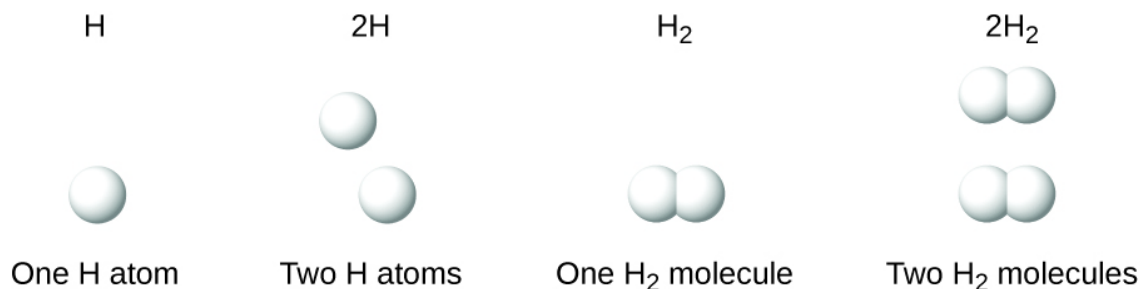
A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

Although many elements consist of discrete, individual atoms, some exist as molecules made up of two or more atoms of the element chemically bonded together. For example, most samples of the elements hydrogen, oxygen, and nitrogen are composed of molecules that contain two atoms each (called diatomic molecules) and thus have the molecular formulas H_2 , O_2 , and N_2 , respectively. Other elements commonly found as diatomic molecules are fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2). The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is S_8 ([link](#)).



A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8 . It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

It is important to note that a subscript following a symbol and a number in front of a symbol do not represent the same thing; for example, H_2 and 2H represent distinctly different species. H_2 is a molecular formula; it represents a diatomic molecule of hydrogen, consisting of two atoms of the element that are chemically bonded together. The expression 2H , on the other hand, indicates two separate hydrogen atoms that are not combined as a unit. The expression 2H_2 represents two molecules of diatomic hydrogen ([link](#)).

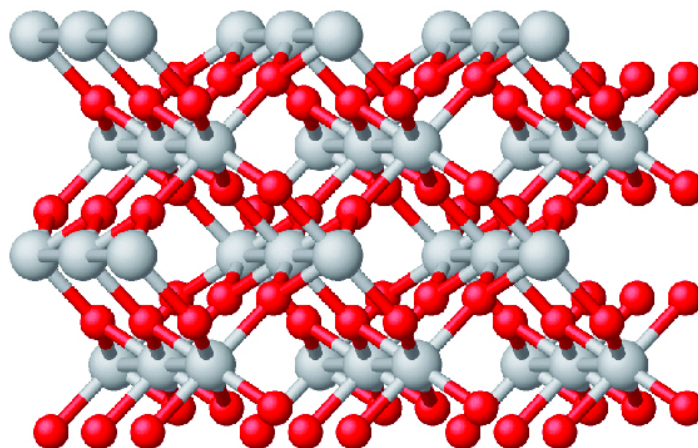


The symbols H , $2H$, H_2 , and $2H_2$ represent very different entities.

Compounds are formed when two or more elements chemically combine, resulting in the formation of bonds. For example, hydrogen and oxygen can react to form water, and sodium and chlorine can react to form table salt. We sometimes describe the composition of these compounds with an **empirical formula**, which indicates the types of atoms present and *the simplest whole-number ratio of the number of atoms (or ions) in the compound*. For example, titanium dioxide (used as pigment in white paint and in the thick, white, blocking type of sunscreen) has an empirical formula of TiO_2 . This identifies the elements titanium (Ti) and oxygen (O) as the constituents of titanium dioxide, and indicates the presence of twice as many atoms of the element oxygen as atoms of the element titanium ([\[link\]](#)).



(a)

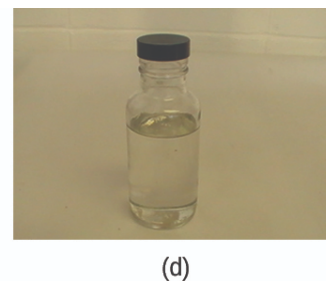
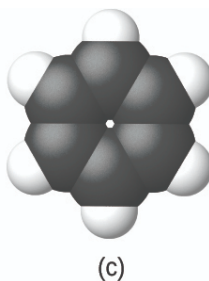
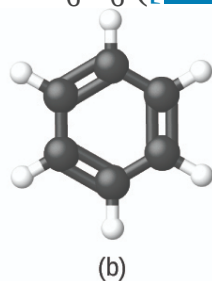
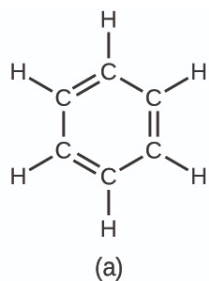


(b)

(a) The white compound titanium dioxide provides effective protection

from the sun. (b) A crystal of titanium dioxide, TiO_2 , contains titanium and oxygen in a ratio of 1 to 2. The titanium atoms are gray and the oxygen atoms are red. (credit a: modification of work by “osseous”/Flickr)

As discussed previously, we can describe a compound with a molecular formula, in which the subscripts indicate the *actual numbers of atoms* of each element in a molecule of the compound. In many cases, the molecular formula of a substance is derived from experimental determination of both its empirical formula and its molecular mass (the sum of atomic masses for all atoms composing the molecule). For example, it can be determined experimentally that benzene contains two elements, carbon (C) and hydrogen (H), and that for every carbon atom in benzene, there is one hydrogen atom. Thus, the empirical formula is CH. An experimental determination of the molecular mass reveals that a molecule of benzene contains six carbon atoms and six hydrogen atoms, so the molecular formula for benzene is C_6H_6 ([link](#)).



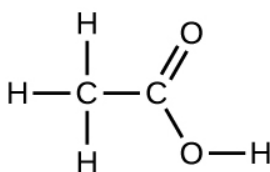
Benzene, C_6H_6 , is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. (credit d: modification of work by Sahar Atwa)

If we know a compound's formula, we can easily determine the empirical formula. (This is somewhat of an academic exercise; the reverse chronology is generally followed in actual practice.) For example, the molecular

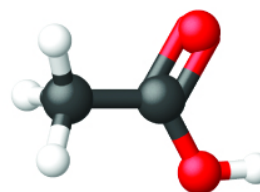
formula for acetic acid, the component that gives vinegar its sharp taste, is $\text{C}_2\text{H}_4\text{O}_2$. This formula indicates that a molecule of acetic acid ([\[link\]](#)) contains two carbon atoms, four hydrogen atoms, and two oxygen atoms. The ratio of atoms is 2:4:2. Dividing by the lowest common denominator (2) gives the simplest, whole-number ratio of atoms, 1:2:1, so the empirical formula is CH_2O . Note that a molecular formula is always a whole-number multiple of an empirical formula.



(a)



(b)



(c)

(a) Vinegar contains acetic acid, $\text{C}_2\text{H}_4\text{O}_2$, which has an empirical formula of CH_2O . It can be represented as (b) a structural formula and (c) as a ball-and-stick model. (credit a: modification of work by “HomeSpot HQ”/Flickr)

Example:

Empirical and Molecular Formulas

Molecules of glucose (blood sugar) contain 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. What are the molecular and empirical formulas of glucose?

Solution

The molecular formula is $\text{C}_6\text{H}_{12}\text{O}_6$ because one molecule actually contains 6 C, 12 H, and 6 O atoms. The simplest whole-number ratio of C to H to O atoms in glucose is 1:2:1, so the empirical formula is CH_2O .

Check Your Learning

A molecule of metaldehyde (a pesticide used for snails and slugs) contains 8 carbon atoms, 16 hydrogen atoms, and 4 oxygen atoms. What are the molecular and empirical formulas of metaldehyde?

Note:

Answer:

Molecular formula, $\text{C}_8\text{H}_{16}\text{O}_4$; empirical formula, $\text{C}_2\text{H}_4\text{O}$

Note:



You can explore [molecule building](#) using an online simulation.

Note:

Lee Cronin

What is it that chemists do? According to Lee Cronin ([\[link\]](#)), chemists make very complicated molecules by “chopping up” small molecules and “reverse engineering” them. He wonders if we could “make a really cool universal chemistry set” by what he calls “app-ing” chemistry. Could we “app” chemistry?

In a 2012 TED talk, Lee describes one fascinating possibility: combining a collection of chemical “inks” with a 3D printer capable of fabricating a

reaction apparatus (tiny test tubes, beakers, and the like) to fashion a “universal toolkit of chemistry.” This toolkit could be used to create custom-tailored drugs to fight a new superbug or to “print” medicine personally configured to your genetic makeup, environment, and health situation. Says Cronin, “What Apple did for music, I’d like to do for the discovery and distribution of prescription drugs.”[\[footnote\]](#) View his [full talk](#) at the TED website.

Lee Cronin, “Print Your Own Medicine,” Talk presented at TED Global 2012, Edinburgh, Scotland, June 2012.

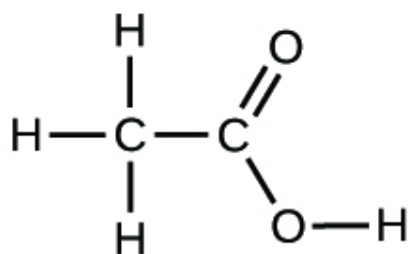


Chemist Lee Cronin has been named one of the UK’s 10 most inspirational scientists. The youngest chair at the University of

Glasgow, Lee runs a large research group, collaborates with many scientists worldwide, has published over 250 papers in top scientific journals, and has given more than 150 invited talks. His research focuses on complex chemical systems and their potential to transform technology, but also branches into nanoscience, solar fuels, synthetic biology, and even artificial life and evolution. (credit: image courtesy of Lee Cronin)

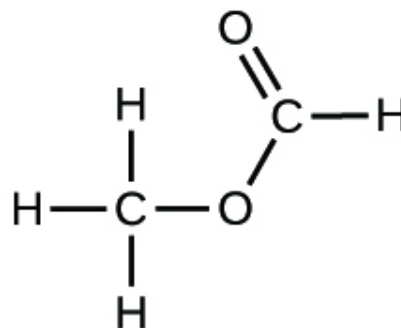
It is important to be aware that it may be possible for the same atoms to be arranged in different ways: Compounds with the same molecular formula may have different atom-to-atom bonding and therefore different structures. For example, could there be another compound with the same formula as acetic acid, $\text{C}_2\text{H}_4\text{O}_2$? And if so, what would be the structure of its molecules?

If you predict that another compound with the formula $\text{C}_2\text{H}_4\text{O}_2$ could exist, then you demonstrated good chemical insight and are correct. Two C atoms, four H atoms, and two O atoms can also be arranged to form a methyl formate, which is used in manufacturing, as an insecticide, and for quick-drying finishes. Methyl formate molecules have one of the oxygen atoms between the two carbon atoms, differing from the arrangement in acetic acid molecules. Acetic acid and methyl formate are examples of **isomers**—compounds with the same chemical formula but different molecular structures ([\[link\]](#)). Note that this small difference in the arrangement of the atoms has a major effect on their respective chemical properties. You would certainly not want to use a solution of methyl formate as a substitute for a solution of acetic acid (vinegar) when you make salad dressing.



Acetic acid
C₂H₄O₂

(a)

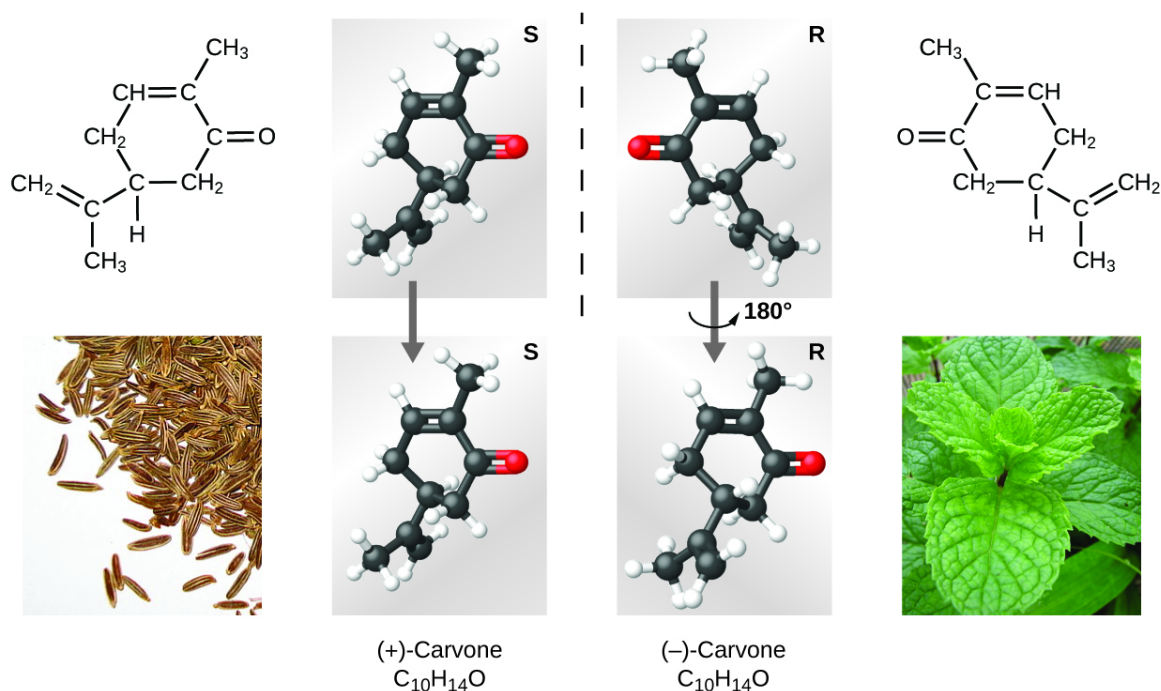


Methyl formate
C₂H₄O₂

(b)

Molecules of (a) acetic acid and methyl formate (b) are structural isomers; they have the same formula (C₂H₄O₂) but different structures (and therefore different chemical properties).

Many types of isomers exist ([\[link\]](#)). Acetic acid and methyl formate are **structural isomers**, compounds in which the molecules differ in how the atoms are connected to each other. There are also various types of **spatial isomers**, in which the relative orientations of the atoms in space can be different. For example, the compound carvone (found in caraway seeds, spearmint, and mandarin orange peels) consists of two isomers that are mirror images of each other. *S*-(+)-carvone smells like caraway, and *R*-(-)-carvone smells like spearmint.



Molecules of carvone are spatial isomers; they only differ in the relative orientations of the atoms in space. (credit bottom left: modification of work by “Miansari66”/Wikimedia Commons; credit bottom right: modification of work by Forest & Kim Starr)

Note:



Select this [link](#) to view an explanation of isomers, spatial isomers, and why they have different smells (select the video titled “Mirror Molecule: Carvone”).

Key Concepts and Summary

A molecular formula uses chemical symbols and subscripts to indicate the exact numbers of different atoms in a molecule or compound. An empirical formula gives the simplest, whole-number ratio of atoms in a compound. A structural formula indicates the bonding arrangement of the atoms in the molecule. Ball-and-stick and space-filling models show the geometric arrangement of atoms in a molecule. Isomers are compounds with the same molecular formula but different arrangements of atoms.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Explain why the symbol for an atom of the element oxygen and the formula for a molecule of oxygen differ.

Solution:

The symbol for the element oxygen, O, represents both the element and one atom of oxygen. A molecule of oxygen, O₂, contains two oxygen atoms; the subscript 2 in the formula must be used to distinguish the diatomic molecule from two single oxygen atoms.

Exercise:

Problem:

Explain why the symbol for the element sulfur and the formula for a molecule of sulfur differ.

Exercise:

Problem:

Write the molecular and empirical formulas of the following compounds:

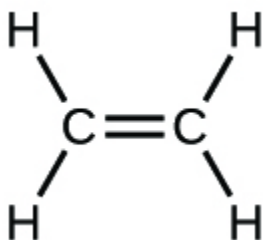
(a)



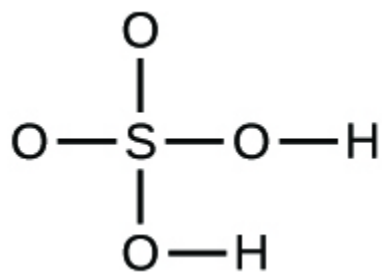
(b)



(c)



(d)



Solution:

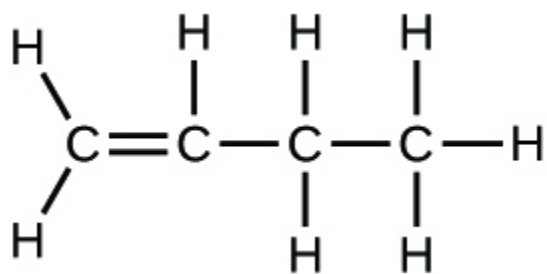
(a) molecular CO_2 , empirical CO_2 ; (b) molecular C_2H_2 , empirical CH ;
(c) molecular C_2H_4 , empirical CH_2 ; (d) molecular H_2SO_4 , empirical
 H_2SO_4

Exercise:

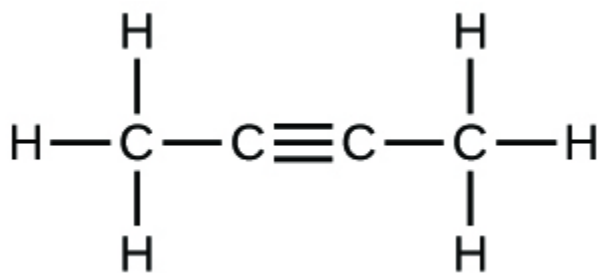
Problem:

Write the molecular and empirical formulas of the following compounds:

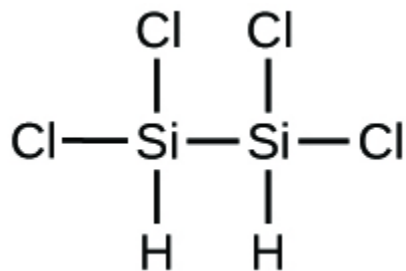
(a)



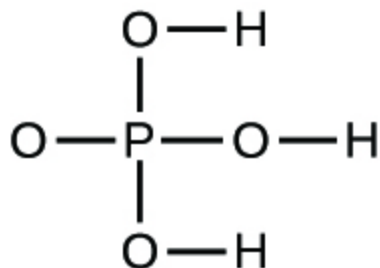
(b)



(c)



(d)



Exercise:

Problem:

Determine the empirical formulas for the following compounds:

- (a) caffeine, $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$
 - (b) fructose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
 - (c) hydrogen peroxide, H_2O_2
 - (d) glucose, $\text{C}_6\text{H}_{12}\text{O}_6$
 - (e) ascorbic acid (vitamin C), $\text{C}_6\text{H}_8\text{O}_6$
-

Solution:

- (a) $\text{C}_4\text{H}_5\text{N}_2\text{O}$; (b) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$; (c) HO ; (d) CH_2O ; (e) $\text{C}_3\text{H}_4\text{O}_3$

Exercise:

Problem:

Determine the empirical formulas for the following compounds:

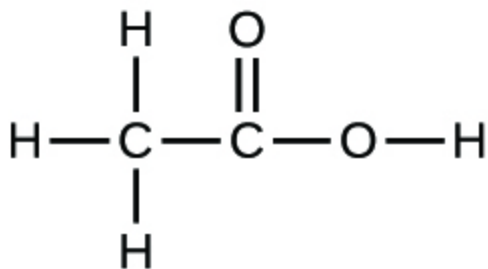
- (a) acetic acid, $\text{C}_2\text{H}_4\text{O}_2$
- (b) citric acid, $\text{C}_6\text{H}_8\text{O}_7$
- (c) hydrazine, N_2H_4
- (d) nicotine, $\text{C}_{10}\text{H}_{14}\text{N}_2$

(e) butane, C_4H_{10}

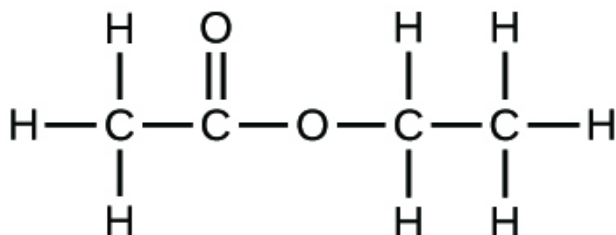
Exercise:

Problem: Write the empirical formulas for the following compounds:

(a)



(b)



Solution:

(a) CH_2O ; (b) C_2H_4O

Exercise:

Problem:

Open the [Build a Molecule simulation](#) and select the “Larger Molecules” tab. Select an appropriate atoms “Kit” to build a molecule with two carbon and six hydrogen atoms. Drag atoms into the space above the “Kit” to make a molecule. A name will appear when you have made an actual molecule that exists (even if it is not the one you want). You can use the scissors tool to separate atoms if you would like to change the connections. Click on “3D” to see the molecule, and look at both the space-filling and ball-and-stick possibilities.

- (a) Draw the structural formula of this molecule and state its name.
- (b) Can you arrange these atoms in any way to make a different compound?

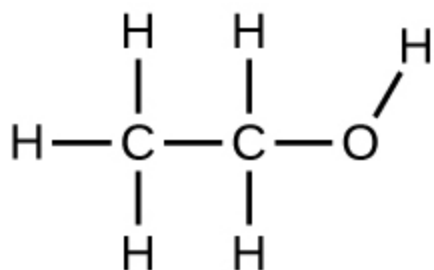
Exercise:**Problem:**

Use the [Build a Molecule simulation](#) to repeat [\[link\]](#), but build a molecule with two carbons, six hydrogens, and one oxygen.

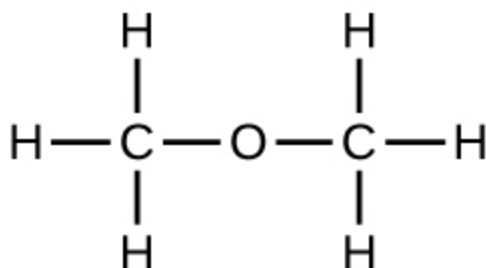
- (a) Draw the structural formula of this molecule and state its name.
- (b) Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.
- (c) How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names).

Solution:

- (a) ethanol



(b) methoxymethane, more commonly known as dimethyl ether



(c) These molecules have the same chemical composition (types and number of atoms) but different chemical structures. They are structural isomers.

Exercise:

Problem:

Use the [Build a Molecule simulation](#) to repeat [\[link\]](#), but build a molecule with three carbons, seven hydrogens, and one chlorine.

(a) Draw the structural formula of this molecule and state its name.

(b) Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.

(c) How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names)?

Glossary

empirical formula

formula showing the composition of a compound given as the simplest whole-number ratio of atoms

isomers

compounds with the same chemical formula but different structures

molecular formula

formula indicating the composition of a molecule of a compound and giving the actual number of atoms of each element in a molecule of the compound.

spatial isomers

compounds in which the relative orientations of the atoms in space differ

structural formula

shows the atoms in a molecule and how they are connected

structural isomer

one of two substances that have the same molecular formula but different physical and chemical properties because their atoms are bonded differently

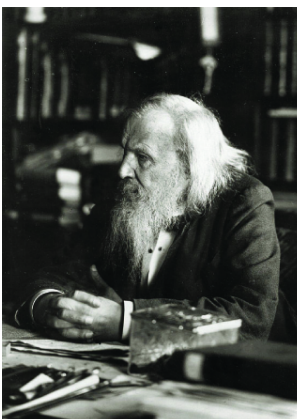
The Periodic Table

By the end of this section, you will be able to:

- State the periodic law and explain the organization of elements in the periodic table
- Predict the general properties of elements based on their location within the periodic table
- Identify metals, nonmetals, and metalloids by their properties and/or location on the periodic table

As early chemists worked to purify ores and discovered more elements, they realized that various elements could be grouped together by their similar chemical behaviors. One such grouping includes lithium (Li), sodium (Na), and potassium (K): These elements all are shiny, conduct heat and electricity well, and have similar chemical properties. A second grouping includes calcium (Ca), strontium (Sr), and barium (Ba), which also are shiny, good conductors of heat and electricity, and have chemical properties in common. However, the specific properties of these two groupings are notably different from each other. For example: Li, Na, and K are much more reactive than are Ca, Sr, and Ba; Li, Na, and K form compounds with oxygen in a ratio of two of their atoms to one oxygen atom, whereas Ca, Sr, and Ba form compounds with one of their atoms to one oxygen atom. Fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) also exhibit similar properties to each other, but these properties are drastically different from those of any of the elements above.

Dimitri Mendeleev in Russia (1869) and Lothar Meyer in Germany (1870) independently recognized that there was a periodic relationship among the properties of the elements known at that time. Both published tables with the elements arranged according to increasing atomic mass. But Mendeleev went one step further than Meyer: He used his table to predict the existence of elements that would have the properties similar to aluminum and silicon, but were yet unknown. The discoveries of gallium (1875) and germanium (1886) provided great support for Mendeleev's work. Although Mendeleev and Meyer had a long dispute over priority, Mendeleev's contributions to the development of the periodic table are now more widely recognized ([link](#)).



(a)

Rechn	Gruppo I. — R ⁰	Gruppo II. — R ⁰	Gruppo III. — R ⁰ ^a	Gruppo IV. RH ^a R ⁰ ^a	Gruppo V. RH ^a R ⁰ ^a	Gruppo VI. RH ^a R ⁰ ^a	Gruppo VII. RH ^a R ⁰ ^a	Gruppo VIII. — R ⁰ ^a
1	II=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

(b)

(a) Dimitri Mendeleev is widely credited with creating (b) the first periodic table of the elements. (credit a: modification of work by Serge Lachinov; credit b: modification of work by “Den fjättrade ankan”/Wikimedia Commons)

By the twentieth century, it became apparent that the periodic relationship involved atomic numbers rather than atomic masses. The modern statement of this relationship, the **periodic law**, is as follows: *the properties of the elements are periodic functions of their atomic numbers*. A modern **periodic table** arranges the elements in increasing order of their atomic numbers and groups atoms with similar properties in the same vertical column ([link](#)). Each box represents an element and contains its atomic number, symbol, average atomic mass, and (sometimes) name. The elements are arranged in seven horizontal rows, called **periods** or **series**, and 18 vertical columns, called **groups**. Groups are labeled at the top of each column. In the United States, the labels traditionally were numerals with capital letters. However, IUPAC recommends that the numbers 1 through 18 be used, and these labels are more common. For the table to fit on a single page, parts of two of the rows, a total of 14 columns, are usually written below the main body of the table.

Period

Group

1

2

13

14

15

16

17

18

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Elements in the periodic table are organized according to their properties.

Many elements differ dramatically in their chemical and physical properties, but some elements are similar in their behaviors. For example, many elements appear shiny, are malleable (able to be deformed without breaking) and ductile (can be drawn into wires), and conduct heat and electricity well. Other elements are not shiny, malleable, or ductile, and are poor conductors of heat and electricity. We can sort the elements into large classes with common properties: **metals** (elements that are shiny, malleable, good conductors of heat and electricity—shaded yellow); **nonmetals** (elements that appear dull, poor conductors of heat and electricity—shaded green); and **metalloids** (elements that conduct heat and electricity

moderately well, and possess some properties of metals and some properties of nonmetals—shaded purple).

The elements can also be classified into the **main-group elements** (or **representative elements**) in the columns labeled 1, 2, and 13–18; the **transition metals** in the columns labeled 3–12; and **inner transition metals** in the two rows at the bottom of the table (the top-row elements are called **lanthanides** and the bottom-row elements are **actinides**; [link](#)). The elements can be subdivided further by more specific properties, such as the composition of the compounds they form. For example, the elements in group 1 (the first column) form compounds that consist of one atom of the element and one atom of hydrogen. These elements (except hydrogen) are known as **alkali metals**, and they all have similar chemical properties. The elements in group 2 (the second column) form compounds consisting of one atom of the element and two atoms of hydrogen: These are called **alkaline earth metals**, with similar properties among members of that group. Other groups with specific names are the **pnictogens** (group 15), **chalcogens** (group 16), **halogens** (group 17), and the **noble gases** (group 18, also known as **inert gases**). The groups can also be referred to by the first element of the group: For example, the chalcogens can be called the oxygen group or oxygen family. Hydrogen is a unique, nonmetallic element with properties similar to both group 1 and group 17 elements. For that reason, hydrogen may be shown at the top of both groups, or by itself.

Periodic Table of the Elements

Group 1	Main group elements																18	
	2											13	14	15	16	17		
A l k a l i m e t a l s	e a r t h a l k a l i n e m e t a l s	3	4	5	6	7	8	9	10	11	12			P n i c t o g e n s	C h a l c o g e n s	H a l o g e n s	N o b l e g a s e s	
		Transition metals																
		Lanthanides																
		Actinides																

The periodic table organizes elements with similar properties into groups.

Note:



Click on this [link](#) for an interactive periodic table, which you can use to explore the properties of the elements (includes podcasts and videos of each element). You may also want to try this [one](#) that shows photos of all the elements.

Example:**Naming Groups of Elements**

Atoms of each of the following elements are essential for life. Give the group name for the following elements:

- (a) chlorine
- (b) calcium
- (c) sodium
- (d) sulfur

Solution

The family names are as follows:

- (a) halogen
- (b) alkaline earth metal
- (c) alkali metal
- (d) chalcogen

Check Your Learning

Give the group name for each of the following elements:

- (a) krypton
- (b) selenium
- (c) barium
- (d) lithium

Note:**Answer:**

(a) noble gas; (b) chalcogen; (c) alkaline earth metal; (d) alkali metal

In studying the periodic table, you might have noticed something about the atomic masses of some of the elements. Element 43 (technetium), element 61 (promethium), and most of the elements with atomic number 84 (polonium) and higher have their atomic mass given in square brackets. This is done for elements that consist entirely of unstable, radioactive isotopes (you will learn more about radioactivity in the nuclear chemistry

chapter). An average atomic weight cannot be determined for these elements because their radioisotopes may vary significantly in relative abundance, depending on the source, or may not even exist in nature. The number in square brackets is the atomic mass number (an approximate atomic mass) of the most stable isotope of that element.

Key Concepts and Summary

The discovery of the periodic recurrence of similar properties among the elements led to the formulation of the periodic table, in which the elements are arranged in order of increasing atomic number in rows known as periods and columns known as groups. Elements in the same group of the periodic table have similar chemical properties. Elements can be classified as metals, metalloids, and nonmetals, or as a main-group elements, transition metals, and inner transition metals. Groups are numbered 1–18 from left to right. The elements in group 1 are known as the alkali metals; those in group 2 are the alkaline earth metals; those in 15 are the pnictogens; those in 16 are the chalcogens; those in 17 are the halogens; and those in 18 are the noble gases.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:

- (a) uranium
- (b) bromine
- (c) strontium
- (d) neon

- (e) gold
 - (f) americium
 - (g) rhodium
 - (h) sulfur
 - (i) carbon
 - (j) potassium
-

Solution:

(a) metal, inner transition metal; (b) nonmetal, representative element; (c) metal, representative element; (d) nonmetal, representative element; (e) metal, transition metal; (f) metal, inner transition metal; (g) metal, transition metal; (h) nonmetal, representative element; (i) nonmetal, representative element; (j) metal, representative element

Exercise:

Problem:

Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:

- (a) cobalt
- (b) europium
- (c) iodine
- (d) indium
- (e) lithium
- (f) oxygen

(g) cadmium

(h) terbium

(i) rhenium

Exercise:

Problem:

Using the periodic table, identify the lightest member of each of the following groups:

(a) noble gases

(b) alkaline earth metals

(c) alkali metals

(d) chalcogens

Solution:

(a) He; (b) Be; (c) Li; (d) O

Exercise:

Problem:

Using the periodic table, identify the heaviest member of each of the following groups:

(a) alkali metals

(b) chalcogens

(c) noble gases

(d) alkaline earth metals

Exercise:

Problem:

Use the periodic table to give the name and symbol for each of the following elements:

- (a) the noble gas in the same period as germanium
 - (b) the alkaline earth metal in the same period as selenium
 - (c) the halogen in the same period as lithium
 - (d) the chalcogen in the same period as cadmium
-

Solution:

- (a) krypton, Kr; (b) calcium, Ca; (c) fluorine, F; (d) tellurium, Te

Exercise:**Problem:**

Use the periodic table to give the name and symbol for each of the following elements:

- (a) the halogen in the same period as the alkali metal with 11 protons
- (b) the alkaline earth metal in the same period with the neutral noble gas with 18 electrons
- (c) the noble gas in the same row as an isotope with 30 neutrons and 25 protons
- (d) the noble gas in the same period as gold

Exercise:**Problem:**

Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

- (a) the alkali metal with 11 protons and a mass number of 23
 - (b) the noble gas element with 75 neutrons in its nucleus and 54 electrons in the neutral atom
 - (c) the isotope with 33 protons and 40 neutrons in its nucleus
 - (d) the alkaline earth metal with 88 electrons and 138 neutrons
-

Solution:

(a) ${}_{11}^{23}\text{Na}$; (b) ${}_{54}^{129}\text{Xe}$; (c) ${}_{33}^{73}\text{As}$; (d) ${}_{88}^{226}\text{Ra}$

Exercise:

Problem:

Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

- (a) the chalcogen with a mass number of 125
- (b) the halogen whose longest-lived isotope is radioactive
- (c) the noble gas, used in lighting, with 10 electrons and 10 neutrons
- (d) the lightest alkali metal with three neutrons

Glossary

actinide

inner transition metal in the bottom of the bottom two rows of the periodic table

alkali metal

element in group 1

alkaline earth metal

element in group 2

chalcogen
element in group 16

group
vertical column of the periodic table

halogen
element in group 17

inert gas
(also, noble gas) element in group 18

inner transition metal
(also, lanthanide or actinide) element in the bottom two rows; if in the first row, also called lanthanide, or if in the second row, also called actinide

lanthanide
inner transition metal in the top of the bottom two rows of the periodic table

main-group element
(also, representative element) element in columns 1, 2, and 12–18

metal
element that is shiny, malleable, good conductor of heat and electricity

metalloid
element that conducts heat and electricity moderately well, and possesses some properties of metals and some properties of nonmetals

noble gas
(also, inert gas) element in group 18

nonmetal
element that appears dull, poor conductor of heat and electricity

period
(also, series) horizontal row of the periodic table

periodic law

properties of the elements are periodic function of their atomic numbers.

periodic table

table of the elements that places elements with similar chemical properties close together

pnictogen

element in group 15

representative element

(also, main-group element) element in columns 1, 2, and 12–18

series

(also, period) horizontal row of the period table

transition metal

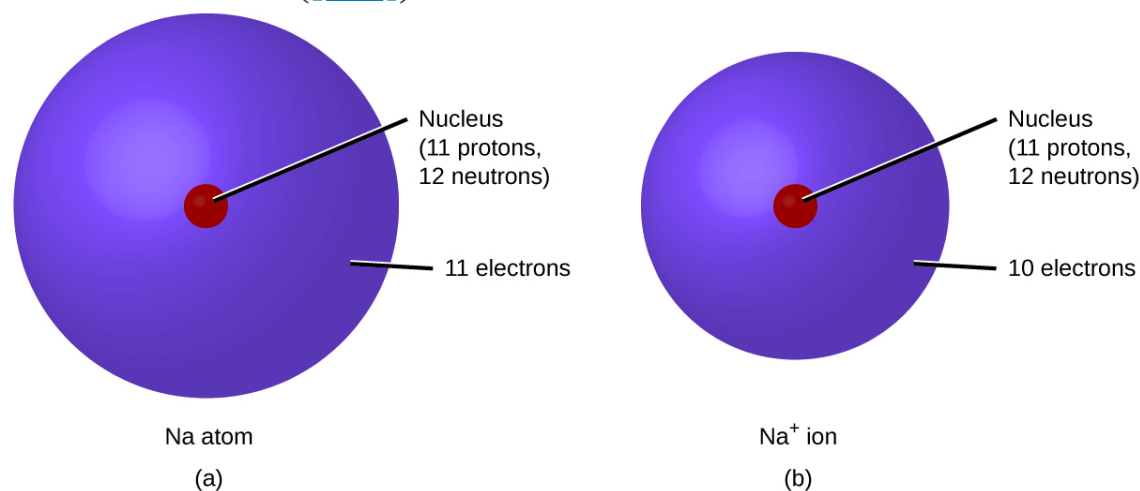
element in columns 3–11

Molecular and Ionic Compounds

By the end of this section, you will be able to:

- Define ionic and molecular (covalent) compounds
- Predict the type of compound formed from elements based on their location within the periodic table
- Determine formulas for simple ionic compounds

In ordinary chemical reactions, the nucleus of each atom (and thus the identity of the element) remains unchanged. Electrons, however, can be added to atoms by transfer from other atoms, lost by transfer to other atoms, or shared with other atoms. The transfer and sharing of electrons among atoms govern the chemistry of the elements. During the formation of some compounds, atoms gain or lose electrons, and form electrically charged particles called ions ([\[link\]](#)).



(a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na^+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.

You can use the periodic table to predict whether an atom will form an anion or a cation, and you can often predict the charge of the resulting ion. Atoms of many main-group metals lose enough electrons to leave them with the same number of electrons as an atom of the preceding noble gas.

To illustrate, an atom of an alkali metal (group 1) loses one electron and forms a cation with a 1+ charge; an alkaline earth metal (group 2) loses two electrons and forms a cation with a 2+ charge, and so on. For example, a neutral calcium atom, with 20 protons and 20 electrons, readily loses two electrons. This results in a cation with 20 protons, 18 electrons, and a 2+ charge. It has the same number of electrons as atoms of the preceding noble gas, argon, and is symbolized Ca^{2+} . The name of a metal ion is the same as the name of the metal atom from which it forms, so Ca^{2+} is called a calcium ion.

When atoms of nonmetal elements form ions, they generally gain enough electrons to give them the same number of electrons as an atom of the next noble gas in the periodic table. Atoms of group 17 gain one electron and form anions with a 1- charge; atoms of group 16 gain two electrons and form ions with a 2- charge, and so on. For example, the neutral bromine atom, with 35 protons and 35 electrons, can gain one electron to provide it with 36 electrons. This results in an anion with 35 protons, 36 electrons, and a 1- charge. It has the same number of electrons as atoms of the next noble gas, krypton, and is symbolized Br^- . (A discussion of the theory supporting the favored status of noble gas electron numbers reflected in these predictive rules for ion formation is provided in a later chapter of this text.)

Note the usefulness of the periodic table in predicting likely ion formation and charge ([\[link\]](#)). Moving from the far left to the right on the periodic table, main-group elements tend to form cations with a charge equal to the group number. That is, group 1 elements form 1+ ions; group 2 elements form 2+ ions, and so on. Moving from the far right to the left on the periodic table, elements often form anions with a negative charge equal to the number of groups moved left from the noble gases. For example, group 17 elements (one group left of the noble gases) form 1- ions; group 16 elements (two groups left) form 2- ions, and so on. This trend can be used as a guide in many cases, but its predictive value decreases when moving toward the center of the periodic table. In fact, transition metals and some other metals often exhibit variable charges that are not predictable by their location in the table. For example, copper can form ions with a 1+ or 2+ charge, and iron can form ions with a 2+ or 3+ charge.

Periodic Table of the Elements

Period	Group 1	Group 2												Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
1																			He
2	Li ⁺	Be ²⁺													C ⁴⁻	N ³⁻	O ²⁻	F ⁻	Ne
3	Na ⁺	Mg ²⁺												Al ³⁺		P ³⁻	S ²⁻	Cl ⁻	Ar
4	K ⁺	Ca ²⁺				Cr ³⁺ Cr ⁶⁺	Mn ²⁺	Fe ²⁺ Fe ³⁺	Co ²⁺	Ni ²⁺	Cu ⁺ Cu ²⁺	Zn ²⁺				As ³⁻	Se ²⁻	Br ⁻	Kr
5	Rb ⁺	Sr ²⁺										Ag ⁺	Cd ²⁺				Te ²⁻	I ⁻	Xe
6	Cs ⁺	Ba ²⁺									Pt ²⁺	Au ⁺ Au ³⁺	Hg ₂ ²⁺ Hg ²⁺					At ⁻	Rn
7	Fr ⁺	Ra ²⁺																	

Note: The table shows a regular pattern of ionic charges for elements in groups 1, 2, 13, 14, 15, 16, 17, and 18. The charges are: Group 1 (+1), Group 2 (+2), Group 13 (+3), Group 14 (0), Group 15 (-3), Group 16 (-2), Group 17 (-1), and Group 18 (0). The charges for elements in groups 3-12 are not shown.

Some elements exhibit a regular pattern of ionic charge when they form ions.

Example:

Composition of Ions

An ion found in some compounds used as antiperspirants contains 13 protons and 10 electrons. What is its symbol?

Solution

Because the number of protons remains unchanged when an atom forms an ion, the atomic number of the element must be 13. Knowing this lets us use the periodic table to identify the element as Al (aluminum). The Al atom has lost three electrons and thus has three more positive charges (13) than it has electrons (10). This is the aluminum cation, Al³⁺.

Check Your Learning

Give the symbol and name for the ion with 34 protons and 36 electrons.

Note:

Answer:

Se^{2-} , the selenide ion

Example:

Formation of Ions

Magnesium and nitrogen react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Solution

Magnesium's position in the periodic table (group 2) tells us that it is a metal. Metals form positive ions (cations). A magnesium atom must lose two electrons to have the same number electrons as an atom of the previous noble gas, neon. Thus, a magnesium atom will form a cation with two fewer electrons than protons and a charge of $2+$. The symbol for the ion is Mg^{2+} , and it is called a magnesium ion.

Nitrogen's position in the periodic table (group 15) reveals that it is a nonmetal. Nonmetals form negative ions (anions). A nitrogen atom must gain three electrons to have the same number of electrons as an atom of the following noble gas, neon. Thus, a nitrogen atom will form an anion with three more electrons than protons and a charge of $3-$. The symbol for the ion is N^{3-} , and it is called a nitride ion.

Check Your Learning

Aluminum and carbon react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Note:

Answer:

Al will form a cation with a charge of $3+$: Al^{3+} , an aluminum ion. Carbon will form an anion with a charge of $4-$: C^{4-} , a carbide ion.

The ions that we have discussed so far are called **monatomic ions**, that is, they are ions formed from only one atom. We also find many **polyatomic ions**. These ions, which act as discrete units, are electrically charged molecules (a group of bonded atoms with an overall charge). Some of the more important polyatomic ions are listed in [\[link\]](#). **Oxyanions** are polyatomic ions that contain one or more oxygen atoms. At this point in your study of chemistry, you should memorize the names, formulas, and charges of the most common polyatomic ions. Because you will use them repeatedly, they will soon become familiar.

Common Polyatomic Ions			
Name	Formula	Related Acid	Formula
ammonium	NH_4^+		
hydronium	H_3O^+		
peroxide	O_2^{2-}		
hydroxide	OH^-		
acetate	CH_3COO^-	acetic acid	CH_3COOH
cyanide	CN^-	hydrocyanic acid	HCN

Common Polyatomic Ions			
Name	Formula	Related Acid	Formula
azide	N_3^-	hydrazoic acid	HN_3
carbonate	CO_3^{2-}	carbonic acid	H_2CO_3
bicarbonate	HCO_3^-		
nitrate	NO_3^-	nitric acid	HNO_3
nitrite	NO_2^-	nitrous acid	HNO_2
sulfate	SO_4^{2-}	sulfuric acid	H_2SO_4
hydrogen sulfate	HSO_4^-		
sulfite	SO_3^{2-}	sulfurous acid	H_2SO_3
hydrogen sulfite	HSO_3^-		
phosphate	PO_4^{3-}	phosphoric acid	H_3PO_4
hydrogen phosphate	HPO_4^{2-}		
dihydrogen phosphate	H_2PO_4^-		
perchlorate	ClO_4^-	perchloric acid	HClO_4

Common Polyatomic Ions			
Name	Formula	Related Acid	Formula
chlorate	ClO_3^-	chloric acid	HClO_3
chlorite	ClO_2^-	chlorous acid	HClO_2
hypochlorite	ClO^-	hypochlorous acid	HClO
chromate	CrO_4^{2-}	chromic acid	$\text{H}_2\text{Cr}_2\text{O}_4$
dichromate	$\text{Cr}_2\text{O}_7^{2-}$	dichromic acid	$\text{H}_2\text{Cr}_2\text{O}_7$
permanganate	MnO_4^-	permanganic acid	HMnO_4

Note that there is a system for naming some polyatomic ions; *-ate* and *-ite* are suffixes designating polyatomic ions containing more or fewer oxygen atoms. *Per-* (short for “hyper”) and *hypo-* (meaning “under”) are prefixes meaning more oxygen atoms than *-ate* and fewer oxygen atoms than *-ite*, respectively. For example, perchlorate is ClO_4^- , chlorate is ClO_3^- , chlorite is ClO_2^- and hypochlorite is ClO^- . Unfortunately, the number of oxygen atoms corresponding to a given suffix or prefix is not consistent; for example, nitrate is NO_3^- while sulfate is SO_4^{2-} . This will be covered in more detail in the next module on nomenclature.

The nature of the attractive forces that hold atoms or ions together within a compound is the basis for classifying chemical bonding. When electrons are transferred and ions form, **ionic bonds** result. Ionic bonds are electrostatic forces of attraction, that is, the attractive forces experienced between objects of opposite electrical charge (in this case, cations and anions). When electrons are “shared” and molecules form, **covalent bonds** result. Covalent bonds are the attractive forces between the positively charged nuclei of the

bonded atoms and one or more pairs of electrons that are located between the atoms. Compounds are classified as ionic or molecular (covalent) on the basis of the bonds present in them.

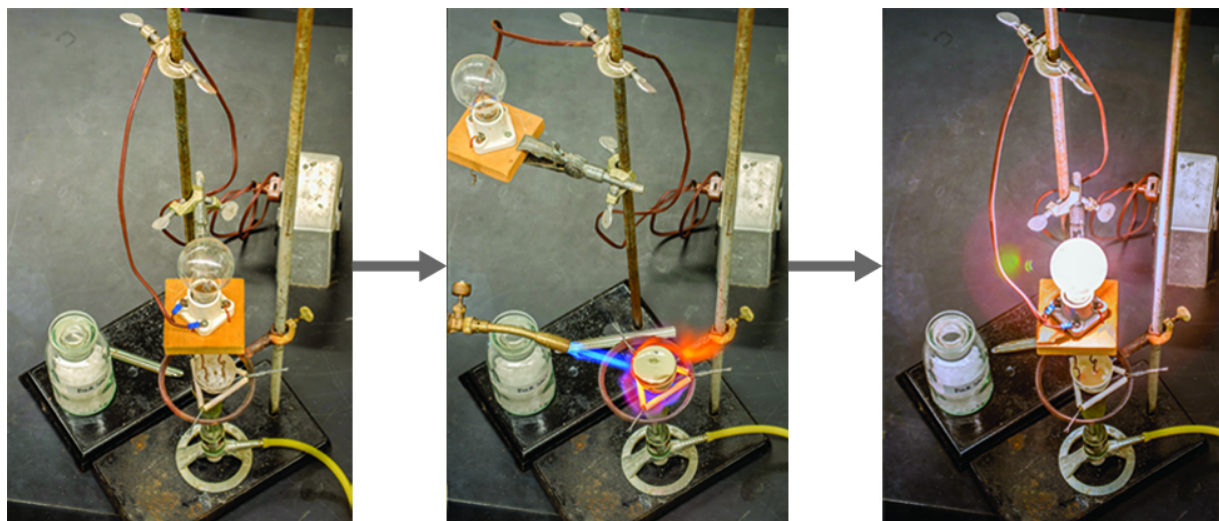
Ionic Compounds

When an element composed of atoms that readily lose electrons (a metal) reacts with an element composed of atoms that readily gain electrons (a nonmetal), a transfer of electrons usually occurs, producing ions. The compound formed by this transfer is stabilized by the electrostatic attractions (ionic bonds) between the ions of opposite charge present in the compound. For example, when each sodium atom in a sample of sodium metal (group 1) gives up one electron to form a sodium cation, Na^+ , and each chlorine atom in a sample of chlorine gas (group 17) accepts one electron to form a chloride anion, Cl^- , the resulting compound, NaCl , is composed of sodium ions and chloride ions in the ratio of one Na^+ ion for each Cl^- ion. Similarly, each calcium atom (group 2) can give up two electrons and transfer one to each of two chlorine atoms to form CaCl_2 , which is composed of Ca^{2+} and Cl^- ions in the ratio of one Ca^{2+} ion to two Cl^- ions.

A compound that contains ions and is held together by ionic bonds is called an **ionic compound**. The periodic table can help us recognize many of the compounds that are ionic: When a metal is combined with one or more nonmetals, the compound is usually ionic. This guideline works well for predicting ionic compound formation for most of the compounds typically encountered in an introductory chemistry course. However, it is not always true (for example, aluminum chloride, AlCl_3 , is not ionic).

You can often recognize ionic compounds because of their properties. Ionic compounds are solids that typically melt at high temperatures and boil at even higher temperatures. For example, sodium chloride melts at $801\text{ }^\circ\text{C}$ and boils at $1413\text{ }^\circ\text{C}$. (As a comparison, the molecular compound water melts at $0\text{ }^\circ\text{C}$ and boils at $100\text{ }^\circ\text{C}$.) In solid form, an ionic compound is not electrically conductive because its ions are unable to flow (“electricity” is the flow of charged particles). When molten, however, it can conduct

electricity because its ions are able to move freely through the liquid ([link](#)).



Sodium chloride melts at 801 °C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)

Note:



Watch this [video](#) to see a mixture of salts melt and conduct electricity.

In every ionic compound, the total number of positive charges of the cations equals the total number of negative charges of the anions. Thus, ionic compounds are electrically neutral overall, even though they contain positive and negative ions. We can use this observation to help us write the formula of an ionic compound. The formula of an ionic compound must have a ratio of ions such that the numbers of positive and negative charges are equal.

Example:

Predicting the Formula of an Ionic Compound

The gemstone sapphire ([link](#)) is mostly a compound of aluminum and oxygen that contains aluminum cations, Al^{3+} , and oxygen anions, O^{2-} . What is the formula of this compound?



Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. (credit: modification of work by Stanislav Doronenko)

Solution

Because the ionic compound must be electrically neutral, it must have the same number of positive and negative charges. Two aluminum ions, each with a charge of $3+$, would give us six positive charges, and three oxide ions, each with a charge of $2-$, would give us six negative charges. The formula would be Al_2O_3 .

Check Your Learning

Predict the formula of the ionic compound formed between the sodium cation, Na^+ , and the sulfide anion, S^{2-} .

Note:

Answer:

Na_2S

Many ionic compounds contain polyatomic ions ([\[link\]](#)) as the cation, the anion, or both. As with simple ionic compounds, these compounds must also be electrically neutral, so their formulas can be predicted by treating the polyatomic ions as discrete units. We use parentheses in a formula to indicate a group of atoms that behave as a unit. For example, the formula for calcium phosphate, one of the minerals in our bones, is $\text{Ca}_3(\text{PO}_4)_2$. This formula indicates that there are three calcium ions (Ca^{2+}) for every two phosphate (PO_4^{3-}) groups. The PO_4^{3-} groups are discrete units, each consisting of one phosphorus atom and four oxygen atoms, and having an overall charge of $3-$. The compound is electrically neutral, and its formula shows a total count of three Ca, two P, and eight O atoms.

Example:

Predicting the Formula of a Compound with a Polyatomic Anion

Baking powder contains calcium dihydrogen phosphate, an ionic compound composed of the ions Ca^{2+} and H_2PO_4^- . What is the formula

of this compound?

Solution

The positive and negative charges must balance, and this ionic compound must be electrically neutral. Thus, we must have two negative charges to balance the 2+ charge of the calcium ion. This requires a ratio of one Ca^{2+} ion to two H_2PO_4^- ions. We designate this by enclosing the formula for the dihydrogen phosphate ion in parentheses and adding a subscript 2. The formula is $\text{Ca}(\text{H}_2\text{PO}_4)_2$.

Check Your Learning

Predict the formula of the ionic compound formed between the lithium ion and the peroxide ion, O_2^{2-} (Hint: Use the periodic table to predict the sign and the charge on the lithium ion.)

Note:

Answer:



Because an ionic compound is not made up of single, discrete molecules, it may not be properly symbolized using a *molecular* formula. Instead, ionic compounds must be symbolized by a formula indicating the *relative numbers* of its constituent ions. For compounds containing only monatomic ions (such as NaCl) and for many compounds containing polyatomic ions (such as CaSO_4), these formulas are just the empirical formulas introduced earlier in this chapter. However, the formulas for some ionic compounds containing polyatomic ions are not empirical formulas. For example, the ionic compound sodium oxalate is comprised of Na^+ and $\text{C}_2\text{O}_4^{2-}$ ions combined in a 2:1 ratio, and its formula is written as $\text{Na}_2\text{C}_2\text{O}_4$. The subscripts in this formula are not the smallest-possible whole numbers, as each can be divided by 2 to yield the empirical formula, NaCO_2 . This is not the accepted formula for sodium oxalate, however, as it does not accurately represent the compound's polyatomic anion, $\text{C}_2\text{O}_4^{2-}$.

Molecular Compounds

Many compounds do not contain ions but instead consist solely of discrete, neutral molecules. These **molecular compounds** (covalent compounds) result when atoms share, rather than transfer (gain or lose), electrons. Covalent bonding is an important and extensive concept in chemistry, and it will be treated in considerable detail in a later chapter of this text. We can often identify molecular compounds on the basis of their physical properties. Under normal conditions, molecular compounds often exist as gases, low-boiling liquids, and low-melting solids, although many important exceptions exist.

Whereas ionic compounds are usually formed when a metal and a nonmetal combine, covalent compounds are usually formed by a combination of nonmetals. Thus, the periodic table can help us recognize many of the compounds that are covalent. While we can use the positions of a compound's elements in the periodic table to predict whether it is ionic or covalent at this point in our study of chemistry, you should be aware that this is a very simplistic approach that does not account for a number of interesting exceptions. Shades of gray exist between ionic and molecular compounds, and you'll learn more about those later.

Example:

Predicting the Type of Bonding in Compounds

Predict whether the following compounds are ionic or molecular:

- (a) KI, the compound used as a source of iodine in table salt
- (b) H_2O_2 , the bleach and disinfectant hydrogen peroxide
- (c) CHCl_3 , the anesthetic chloroform
- (d) Li_2CO_3 , a source of lithium in antidepressants

Solution

- (a) Potassium (group 1) is a metal, and iodine (group 17) is a nonmetal; KI is predicted to be ionic.
- (b) Hydrogen (group 1) is a nonmetal, and oxygen (group 16) is a nonmetal; H_2O_2 is predicted to be molecular.

(c) Carbon (group 14) is a nonmetal, hydrogen (group 1) is a nonmetal, and chlorine (group 17) is a nonmetal; CHCl_3 is predicted to be molecular.

(d) Lithium (group 1) is a metal, and carbonate is a polyatomic ion; Li_2CO_3 is predicted to be ionic.

Check Your Learning

Using the periodic table, predict whether the following compounds are ionic or covalent:

(a) SO_2

(b) CaF_2

(c) N_2H_4

(d) $\text{Al}_2(\text{SO}_4)_3$

Note:

Answer:

(a) molecular; (b) ionic; (c) molecular; (d) ionic

Key Concepts and Summary

Metals (particularly those in groups 1 and 2) tend to lose the number of electrons that would leave them with the same number of electrons as in the preceding noble gas in the periodic table. By this means, a positively charged ion is formed. Similarly, nonmetals (especially those in groups 16 and 17, and, to a lesser extent, those in Group 15) can gain the number of electrons needed to provide atoms with the same number of electrons as in the next noble gas in the periodic table. Thus, nonmetals tend to form negative ions. Positively charged ions are called cations, and negatively charged ions are called anions. Ions can be either monatomic (containing only one atom) or polyatomic (containing more than one atom).

Compounds that contain ions are called ionic compounds. Ionic compounds generally form from metals and nonmetals. Compounds that do not contain

ions, but instead consist of atoms bonded tightly together in molecules (uncharged groups of atoms that behave as a single unit), are called covalent compounds. Covalent compounds usually form from two nonmetals.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Using the periodic table, predict whether the following chlorides are ionic or covalent: KCl, NCl₃, ICl, MgCl₂, PCl₅, and CCl₄.

Solution:

Ionic: KCl, MgCl₂; Covalent: NCl₃, ICl, PCl₅, CCl₄

Exercise:

Problem:

Using the periodic table, predict whether the following chlorides are ionic or covalent: SiCl₄, PCl₃, CaCl₂, CsCl, CuCl₂, and CrCl₃.

Exercise:

Problem:

For each of the following compounds, state whether it is ionic or covalent. If it is ionic, write the symbols for the ions involved:

(a) NF₃

(b) BaO

(c) (NH₄)₂CO₃

(d) Sr(H₂PO₄)₂

(e) IBr

(f) Na_2O

Solution:

(a) covalent; (b) ionic, Ba^{2+} , O^{2-} ; (c) ionic, NH_4^+ , CO_3^{2-} ; (d) ionic, Sr^{2+} , H_2PO_4^- ; (e) covalent; (f) ionic, Na^+ , O^{2-}

Exercise:

Problem:

For each of the following compounds, state whether it is ionic or covalent, and if it is ionic, write the symbols for the ions involved:

(a) KClO_4

(b) $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$

(c) H_2S

(d) Ag_2S

(e) N_2Cl_4

(f) $\text{Co}(\text{NO}_3)_2$

Exercise:

Problem:

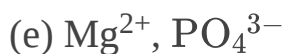
For each of the following pairs of ions, write the formula of the compound they will form:

(a) Ca^{2+} , S^{2-}

(b) NH_4^+ , SO_4^{2-}

(c) Al^{3+} , Br^-

(d) Na^+ , HPO_4^{2-}



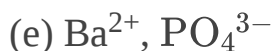
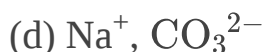
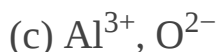
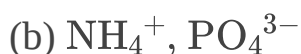
Solution:



Exercise:

Problem:

For each of the following pairs of ions, write the formula of the compound they will form:



Glossary

covalent bond

attractive force between the nuclei of a molecule's atoms and pairs of electrons between the atoms

covalent compound

(also, molecular compound) composed of molecules formed by atoms of two or more different elements

ionic bond

electrostatic forces of attraction between the oppositely charged ions of an ionic compound

ionic compound

compound composed of cations and anions combined in ratios,
yielding an electrically neutral substance

molecular compound

(also, covalent compound) composed of molecules formed by atoms of
two or more different elements

monatomic ion

ion composed of a single atom

oxyanion

polyatomic anion composed of a central atom bonded to oxygen atoms

polyatomic ion

ion composed of more than one atom

Chemical Nomenclature

By the end of this module, you will be able to:

- Derive names for common types of inorganic compounds using a systematic approach

Nomenclature, a collection of rules for naming things, is important in science and in many other situations. This module describes an approach that is used to name simple ionic and molecular compounds, such as NaCl, CaCO₃, and N₂O₄. The simplest of these are **binary compounds**, those containing only two elements, but we will also consider how to name ionic compounds containing polyatomic ions, and one specific, very important class of compounds known as acids (subsequent chapters in this text will focus on these compounds in great detail). We will limit our attention here to inorganic compounds, compounds that are composed principally of elements other than carbon, and will follow the nomenclature guidelines proposed by IUPAC. The rules for organic compounds, in which carbon is the principle element, will be treated in a later chapter on organic chemistry.

Ionic Compounds

To name an inorganic compound, we need to consider the answers to several questions. First, is the compound ionic or molecular? If the compound is ionic, does the metal form ions of only one type (fixed charge) or more than one type (variable charge)? Are the ions monatomic or polyatomic? If the compound is molecular, does it contain hydrogen? If so, does it also contain oxygen? From the answers we derive, we place the compound in an appropriate category and then name it accordingly.

Compounds Containing Only Monatomic Ions

The name of a binary compound containing monatomic ions consists of the name of the cation (the name of the metal) followed by the name of the anion (the name of the nonmetallic element with its ending replaced by the suffix *-ide*). Some examples are given in [\[link\]](#).

Names of Some Ionic Compounds	
NaCl, sodium chloride	Na ₂ O, sodium oxide
KBr, potassium bromide	CdS, cadmium sulfide
CaI ₂ , calcium iodide	Mg ₃ N ₂ , magnesium nitride
CsF, cesium fluoride	Ca ₃ P ₂ , calcium phosphide
LiCl, lithium chloride	Al ₄ C ₃ , aluminum carbide

Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, i.e. by naming first the cation and then the anion. Examples are shown in [\[link\]](#).

Names of Some Polyatomic Ionic Compounds	
KC ₂ H ₃ O ₂ , potassium acetate	NH ₄ Cl, ammonium chloride
NaHCO ₃ , sodium bicarbonate	CaSO ₄ , calcium sulfate
Al ₂ (CO ₃) ₃ , aluminum carbonate	Mg ₃ (PO ₄) ₂ , magnesium phosphate

Note:

Ionic Compounds in Your Cabinets

Every day you encounter and use a large number of ionic compounds. Some of these compounds, where they are found, and what they are used for are listed in [\[link\]](#). Look at the label or ingredients list on the various products that you use during the next few days, and see if you run into any of those in this table, or find other ionic compounds that you could now name or write as a formula.

Everyday Ionic Compounds

Ionic Compound	Use
NaCl, sodium chloride	ordinary table salt
KI, potassium iodide	added to “iodized” salt for thyroid health
NaF, sodium fluoride	ingredient in toothpaste
NaHCO ₃ , sodium bicarbonate	baking soda; used in cooking (and as antacid)
Na ₂ CO ₃ , sodium carbonate	washing soda; used in cleaning agents
NaOCl, sodium hypochlorite	active ingredient in household bleach
CaCO ₃ calcium carbonate	ingredient in antacids
Mg(OH) ₂ , magnesium hydroxide	ingredient in antacids

Everyday Ionic Compounds	
Ionic Compound	Use
$\text{Al}(\text{OH})_3$, aluminum hydroxide	ingredient in antacids
NaOH , sodium hydroxide	lye; used as drain cleaner
K_3PO_4 , potassium phosphate	food additive (many purposes)
MgSO_4 , magnesium sulfate	added to purified water
Na_2HPO_4 , sodium hydrogen phosphate	anti-caking agent; used in powdered products
Na_2SO_3 , sodium sulfite	preservative

Compounds Containing a Metal Ion with a Variable Charge

Most of the transition metals can form two or more cations with different charges. Compounds of these metals with nonmetals are named with the same method as compounds in the first category, except the charge of the metal ion is specified by a Roman numeral in parentheses after the name of the metal. The charge of the metal ion is determined from the formula of the compound and the charge of the anion. For example, consider binary ionic compounds of iron and chlorine. Iron typically exhibits a charge of either $2+$ or $3+$ (see [\[link\]](#)), and the two corresponding compound formulas are FeCl_2 and FeCl_3 . The simplest name, “iron chloride,” will, in this case, be ambiguous, as it does not distinguish between these two compounds. In cases like this, the charge of the metal ion is included as a Roman numeral in parentheses immediately following the metal name. These two compounds are then unambiguously named iron(II) chloride and iron(III) chloride, respectively. Other examples are provided in [\[link\]](#).

Names of Some Transition Metal Ionic Compounds	
Transition Metal Ionic Compound	Name
FeCl_3	iron(III) chloride
Hg_2O	mercury(I) oxide
HgO	mercury(II) oxide
$\text{Cu}_3(\text{PO}_4)_2$	copper(II) phosphate

Out-of-date nomenclature used the suffixes *-ic* and *-ous* to designate metals with higher and lower charges, respectively: Iron(III) chloride, FeCl_3 , was previously called ferric chloride, and iron(II) chloride, FeCl_2 , was known as ferrous chloride. Though this naming convention has been largely abandoned by the scientific community, it remains in use by some segments of industry. For example, you may see the words *stannous fluoride* on a tube of toothpaste. This represents the formula SnF_2 , which is more properly named tin(II) fluoride. The other fluoride of tin is SnF_4 , which was previously called stannic fluoride but is now named tin(IV) fluoride.

Example:

Naming Ionic Compounds

Name the following ionic compounds, which contain a metal that can have more than one ionic charge:

- (a) Fe_2S_3
- (b) CuSe
- (c) GaN
- (d) CrCl_3
- (e) $\text{Ti}_2(\text{SO}_4)_3$

Solution

The anions in these compounds have a fixed negative charge (S^{2-} , Se^{2-} , N^{3-} , Cl^- , and SO_4^{2-}), and the compounds must be neutral. Because the

total number of positive charges in each compound must equal the total number of negative charges, the positive ions must be Fe^{3+} , Cu^{2+} , Ga^{3+} , Cr^{3+} , and Ti^{3+} . These charges are used in the names of the metal ions:

- (a) iron(III) sulfide
- (b) copper(II) selenide
- (c) gallium(III) nitride
- (d) chromium(III) chloride
- (e) titanium(III) sulfate

Check Your Learning

Write the formulas of the following ionic compounds:

- (a) chromium(III) phosphide
- (b) mercury(II) sulfide
- (c) manganese(II) phosphate
- (d) copper(I) oxide
- (e) chromium(VI) fluoride

Note:

Answer:

(a) CrP ; (b) HgS ; (c) $\text{Mn}_3(\text{PO}_4)_2$; (d) Cu_2O ; (e) CrF_6

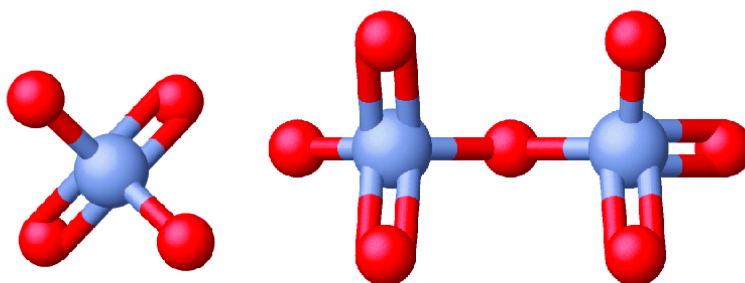
Note:

Erin Brokovich and Chromium Contamination

In the early 1990s, legal file clerk Erin Brockovich ([\[link\]](#)) discovered a high rate of serious illnesses in the small town of Hinckley, California. Her investigation eventually linked the illnesses to groundwater contaminated by Cr(VI) used by Pacific Gas & Electric (PG&E) to fight corrosion in a nearby natural gas pipeline. As dramatized in the film *Erin Brokovich* (for which Julia Roberts won an Oscar), Erin and lawyer Edward Masry sued PG&E for contaminating the water near Hinckley in 1993. The settlement they won in 1996—\$333 million—was the largest amount ever awarded for a direct-action lawsuit in the US at that time.



(a)



(b)

(a) Erin Brockovich found that Cr(VI), used by PG&E, had contaminated the Hinckley, California, water supply. (b) The Cr(VI) ion is often present in water as the polyatomic ions chromate, CrO_4^{2-} (left), and dichromate, $\text{Cr}_2\text{O}_7^{2-}$ (right).

Chromium compounds are widely used in industry, such as for chrome plating, in dye-making, as preservatives, and to prevent corrosion in cooling tower water, as occurred near Hinckley. In the environment, chromium exists primarily in either the Cr(III) or Cr(VI) forms. Cr(III), an ingredient of many vitamin and nutritional supplements, forms compounds that are not very soluble in water, and it has low toxicity. But Cr(VI) is much more toxic and forms compounds that are reasonably soluble in water. Exposure to small amounts of Cr(VI) can lead to damage of the respiratory, gastrointestinal, and immune systems, as well as the kidneys, liver, blood, and skin.

Despite cleanup efforts, Cr(VI) groundwater contamination remains a problem in Hinckley and other locations across the globe. A 2010 study by the Environmental Working Group found that of 35 US cities tested, 31 had higher levels of Cr(VI) in their tap water than the public health goal of 0.02 parts per billion set by the California Environmental Protection Agency.

Molecular (Covalent) Compounds

The bonding characteristics of inorganic molecular compounds are different from ionic compounds, and they are named using a different system as well. The charges of cations and anions dictate their ratios in ionic compounds, so specifying the names of the ions provides sufficient information to determine chemical formulas. However, because covalent bonding allows for significant variation in the combination ratios of the atoms in a molecule, the names for molecular compounds must explicitly identify these ratios.

Compounds Composed of Two Elements

When two nonmetallic elements form a molecular compound, several combination ratios are often possible. For example, carbon and oxygen can form the compounds CO and CO₂. Since these are different substances with different properties, they cannot both have the same name (they cannot both be called carbon oxide). To deal with this situation, we use a naming method that is somewhat similar to that used for ionic compounds, but with added prefixes to specify the numbers of atoms of each element. The name of the more metallic element (the one farther to the left and/or bottom of the periodic table) is first, followed by the name of the more nonmetallic element (the one farther to the right and/or top) with its ending changed to the suffix *-ide*. The numbers of atoms of each element are designated by the Greek prefixes shown in [\[link\]](#).

Nomenclature Prefixes				
Number	Prefix		Number	Prefix
1 (sometimes omitted)	mono-		6	hexa-
2	di-		7	hepta-

Nomenclature Prefixes				
Number	Prefix		Number	Prefix
3	tri-		8	octa-
4	tetra-		9	nona-
5	penta-		10	deca-

When only one atom of the first element is present, the prefix *mono-* is usually deleted from that part. Thus, CO is named carbon monoxide, and CO₂ is called carbon dioxide. When two vowels are adjacent, the *a* in the Greek prefix is usually dropped. Some other examples are shown in [\[link\]](#).

Names of Some Molecular Compounds Composed of Two Elements				
Compound	Name		Compound	Name
SO ₂	sulfur dioxide		BCl ₃	boron trichloride
SO ₃	sulfur trioxide		SF ₆	sulfur hexafluoride
NO ₂	nitrogen dioxide		PF ₅	phosphorus pentafluoride
N ₂ O ₄	dinitrogen tetroxide		P ₄ O ₁₀	tetraphosphorus decaoxide

Names of Some Molecular Compounds Composed of Two Elements				
Compound	Name		Compound	Name
N_2O_5	dinitrogen pentoxide		IF_7	iodine heptafluoride

There are a few common names that you will encounter as you continue your study of chemistry. For example, although NO is often called nitric oxide, its proper name is nitrogen monoxide. Similarly, N_2O is known as nitrous oxide even though our rules would specify the name dinitrogen monoxide. (And H_2O is usually called water, not dihydrogen monoxide.) You should commit to memory the common names of compounds as you encounter them.

Example:

Naming Covalent Compounds

Name the following covalent compounds:

- (a) SF_6
- (b) N_2O_3
- (c) Cl_2O_7
- (d) P_4O_6

Solution

Because these compounds consist solely of nonmetals, we use prefixes to designate the number of atoms of each element:

- (a) sulfur hexafluoride
- (b) dinitrogen trioxide
- (c) dichlorine heptoxide
- (d) tetraphosphorus hexoxide

Check Your Learning

Write the formulas for the following compounds:

- (a) phosphorus pentachloride
- (b) dinitrogen monoxide
- (c) iodine heptafluoride
- (d) carbon tetrachloride

Note:

Answer:

(a) PCl_5 ; (b) N_2O ; (c) IF_7 ; (d) CCl_4

Note:



The following [website](#) provides practice with naming chemical compounds and writing chemical formulas. You can choose binary, polyatomic, and variable charge ionic compounds, as well as molecular compounds.

Binary Acids

Some compounds containing hydrogen are members of an important class of substances known as acids. The chemistry of these compounds is explored in more detail in later chapters of this text, but for now, it will suffice to note that many acids release hydrogen ions, H^+ , when dissolved in water. To denote this distinct chemical property, a mixture of water with an acid is given a name derived from the compound's name. If the compound is a **binary acid** (comprised of hydrogen and one other nonmetallic element):

1. The word “hydrogen” is changed to the prefix *hydro-*
2. The other nonmetallic element name is modified by adding the suffix *-ic*
3. The word “acid” is added as a second word

For example, when the gas HCl (hydrogen chloride) is dissolved in water, the solution is called *hydrochloric acid*. Several other examples of this nomenclature are shown in [\[link\]](#).

Names of Some Simple Acids	
Name of Gas	Name of Acid
HF(<i>g</i>), hydrogen fluoride	HF(<i>aq</i>), hydrofluoric acid
HCl(<i>g</i>), hydrogen chloride	HCl(<i>aq</i>), hydrochloric acid
HBr(<i>g</i>), hydrogen bromide	HBr(<i>aq</i>), hydrobromic acid
HI(<i>g</i>), hydrogen iodide	HI(<i>aq</i>), hydroiodic acid
H ₂ S(<i>g</i>), hydrogen sulfide	H ₂ S(<i>aq</i>), hydrosulfuric acid

Oxyacids

Many compounds containing three or more elements (such as organic compounds or coordination compounds) are subject to specialized nomenclature rules that you will learn later. However, we will briefly discuss the important compounds known as **oxyacids**, compounds that contain hydrogen, oxygen, and at least one other element, and are bonded in such a way as to impart acidic properties to the compound (you will learn the details of this in a later chapter). Typical oxyacids consist of hydrogen combined with a polyatomic, oxygen-containing ion. To name oxyacids:

1. Omit “hydrogen”
2. Start with the root name of the anion

3. Replace *–ate* with *–ic*, or *–ite* with *–ous*
4. Add “acid”

For example, consider H_2CO_3 (which you might be tempted to call “hydrogen carbonate”). To name this correctly, “hydrogen” is omitted; the *–ate* of carbonate is replaced with *–ic*; and acid is added—so its name is carbonic acid. Other examples are given in [\[link\]](#). There are some exceptions to the general naming method (e.g., H_2SO_4 is called sulfuric acid, not sulfic acid, and H_2SO_3 is sulfurous, not sulfous, acid).

Names of Common Oxyacids		
Formula	Anion Name	Acid Name
$\text{HC}_2\text{H}_3\text{O}_2$	acetate	acetic acid
HNO_3	nitrate	nitric acid
HNO_2	nitrite	nitrous acid
HClO_4	perchlorate	perchloric acid
H_2CO_3	carbonate	carbonic acid
H_2SO_4	sulfate	sulfuric acid
H_2SO_3	sulfite	sulfurous acid
H_3PO_4	phosphate	phosphoric acid

Key Concepts and Summary

Chemists use nomenclature rules to clearly name compounds. Ionic and molecular compounds are named using somewhat-different methods. Binary ionic compounds typically consist of a metal and a nonmetal. The name of the metal is written first, followed by the name of the nonmetal with its ending changed to *-ide*. For example, K_2O is called potassium oxide. If the metal can form ions with different charges, a Roman numeral in parentheses follows the name of the metal to specify its charge. Thus, FeCl_2 is iron(II) chloride and FeCl_3 is iron(III) chloride. Some compounds contain polyatomic ions; the names of common polyatomic ions should be memorized. Molecular compounds can form compounds with different ratios of their elements, so prefixes are used to specify the numbers of atoms of each element in a molecule of the compound. Examples include SF_6 , sulfur hexafluoride, and N_2O_4 , dinitrogen tetroxide. Acids are an important class of compounds containing hydrogen and having special nomenclature rules. Binary acids are named using the prefix *hydro-*, changing the *-ide* suffix to *-ic*, and adding “acid;” HCl is hydrochloric acid. Oxyacids are named by changing the ending of the anion (*-ate* to *-ic* and *-ite* to *-ous*), and adding “acid;” H_2CO_3 is carbonic acid.

Chemistry End of Chapter Exercises

Exercise:

Problem: Name the following compounds:

- (a) CsCl
- (b) BaO
- (c) K_2S
- (d) BeCl_2
- (e) HBr
- (f) AlF_3

Solution:

(a) cesium chloride; (b) barium oxide; (c) potassium sulfide; (d) beryllium chloride; (e) hydrogen bromide; (f) aluminum fluoride

Exercise:

Problem: Name the following compounds:

- (a) NaF
- (b) Rb₂O
- (c) BCl₃
- (d) H₂Se
- (e) P₄O₆
- (f) ICl₃

Exercise:

Problem: Write the formulas of the following compounds:

- (a) rubidium bromide
- (b) magnesium selenide
- (c) sodium oxide
- (d) calcium chloride
- (e) hydrogen fluoride
- (f) gallium phosphide
- (g) aluminum bromide

(h) ammonium sulfate

Solution:

(a) RbBr; (b) MgSe; (c) Na₂O; (d) CaCl₂; (e) HF; (f) GaP; (g) AlBr₃;
(h) (NH₄)₂SO₄

Exercise:

Problem: Write the formulas of the following compounds:

- (a) lithium carbonate
- (b) sodium perchlorate
- (c) barium hydroxide
- (d) ammonium carbonate
- (e) sulfuric acid
- (f) calcium acetate
- (g) magnesium phosphate
- (h) sodium sulfite

Exercise:

Problem: Write the formulas of the following compounds:

- (a) chlorine dioxide
- (b) dinitrogen tetroxide
- (c) potassium phosphide
- (d) silver(I) sulfide
- (e) aluminum nitride

(f) silicon dioxide

Solution:

(a) ClO_2 ; (b) N_2O_4 ; (c) K_3P ; (d) Ag_2S ; (e) AlN ; (f) SiO_2

Exercise:

Problem: Write the formulas of the following compounds:

- (a) barium chloride
- (b) magnesium nitride
- (c) sulfur dioxide
- (d) nitrogen trichloride
- (e) dinitrogen trioxide
- (f) tin(IV) chloride

Exercise:

Problem:

Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:

- (a) Cr_2O_3
 - (b) FeCl_2
 - (c) CrO_3
 - (d) TiCl_4
 - (e) CoO
 - (f) MoS_2
-

Solution:

(a) chromium(III) oxide; (b) iron(II) chloride; (c) chromium(VI) oxide;
(d) titanium(IV) chloride; (e) cobalt(II) oxide; (f) molybdenum(IV)
sulfide

Exercise:**Problem:**

Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:

(a) NiCO_3

(b) MoO_3

(c) $\text{Co}(\text{NO}_3)_2$

(d) V_2O_5

(e) MnO_2

(f) Fe_2O_3

Exercise:**Problem:**

The following ionic compounds are found in common household products. Write the formulas for each compound:

(a) potassium phosphate

(b) copper(II) sulfate

(c) calcium chloride

(d) titanium(IV) oxide

(e) ammonium nitrate

(f) sodium bisulfate (the common name for sodium hydrogen sulfate)

Solution:

(a) K_3PO_4 ; (b) CuSO_4 ; (c) CaCl_2 ; (d) TiO_2 ; (e) NH_4NO_3 ; (f) NaHSO_4

Exercise:

Problem:

The following ionic compounds are found in common household products. Name each of the compounds:

(a) $\text{Ca}(\text{H}_2\text{PO}_4)_2$

(b) FeSO_4

(c) CaCO_3

(d) MgO

(e) NaNO_2

(f) KI

Exercise:

Problem: What are the IUPAC names of the following compounds?

(a) manganese dioxide

(b) mercurous chloride (Hg_2Cl_2)

(c) ferric nitrate [$\text{Fe}(\text{NO}_3)_3$]

(d) titanium tetrachloride

(e) cupric bromide (CuBr_2)

Solution:

(a) manganese(IV) oxide; (b) mercury(I) chloride; (c) iron(III) nitrate;
(d) titanium(IV) chloride; (e) copper(II) bromide

Glossary

binary acid

compound that contains hydrogen and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

binary compound

compound containing two different elements.

nomenclature

system of rules for naming objects of interest

oxyacid

compound that contains hydrogen, oxygen, and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

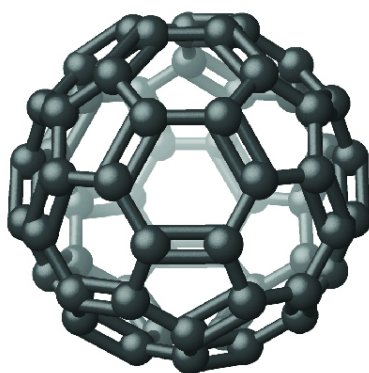
Introduction

class="introduction"

- Ionic Bonding
- Covalent Bonding
- Lewis Symbols and Structures
- Formal Charges and Resonance
- Strengths of Ionic and Covalent Bonds
- Molecular Structure and Polarity

Nicknamed
“buckyballs,”
buckminsterfullerene
molecules (C_{60})
contain only carbon
atoms. Here they are
shown in a ball-and-
stick model (left).
These molecules
have single and
double carbon-carbon
bonds arranged to
form a geometric
framework of
hexagons and
pentagons, similar to
the pattern on a
soccer ball (center).
This unconventional
molecular structure is
named after architect
R. Buckminster
Fuller, whose
innovative designs
combined simple
geometric shapes to

create large, strong structures such as this weather radar dome near Tucson, Arizona (right). (credit middle: modification of work by “Petey21”/Wikimedia Commons; credit right: modification of work by Bill Morrow)



It has long been known that pure carbon occurs in different forms (allotropes) including graphite and diamonds. But it was not until 1985 that a new form of carbon was recognized: buckminsterfullerene, commonly known as a “buckyball.” This molecule was named after the architect and inventor R. Buckminster Fuller (1895–1983), whose signature architectural design was the geodesic dome, characterized by a lattice shell structure supporting a spherical surface. Experimental evidence revealed the formula, C_{60} , and then scientists determined how 60 carbon atoms could form one symmetric, stable molecule. They were guided by bonding theory—the topic of this chapter—which explains how individual atoms connect to form more complex structures.

Ionic Bonding

By the end of this section, you will be able to:

- Explain the formation of cations, anions, and ionic compounds
- Predict the charge of common metallic and nonmetallic elements, and write their electron configurations

As you have learned, ions are atoms or molecules bearing an electrical charge. A cation (a positive ion) forms when a neutral atom loses one or more electrons from its valence shell, and an anion (a negative ion) forms when a neutral atom gains one or more electrons in its valence shell.

Compounds composed of ions are called ionic compounds (or salts), and their constituent ions are held together by **ionic bonds**: electrostatic forces of attraction between oppositely charged cations and anions. The properties of ionic compounds shed some light on the nature of ionic bonds. Ionic solids exhibit a crystalline structure and tend to be rigid and brittle; they also tend to have high melting and boiling points, which suggests that ionic bonds are very strong. Ionic solids are also poor conductors of electricity for the same reason—the strength of ionic bonds prevents ions from moving freely in the solid state. Most ionic solids, however, dissolve readily in water. Once dissolved or melted, ionic compounds are excellent conductors of electricity and heat because the ions can move about freely.

Neutral atoms and their associated ions have very different physical and chemical properties. Sodium *atoms* form sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water. Chlorine *atoms* form chlorine gas, Cl_2 , a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium *cations* and chloride *anions* ([\[link\]](#)). The compound composed of these ions exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride simply dissolves in water.



(a)



(b)



(c)

(a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). (credit a: modification of work by “Jurii”/Wikimedia Commons)

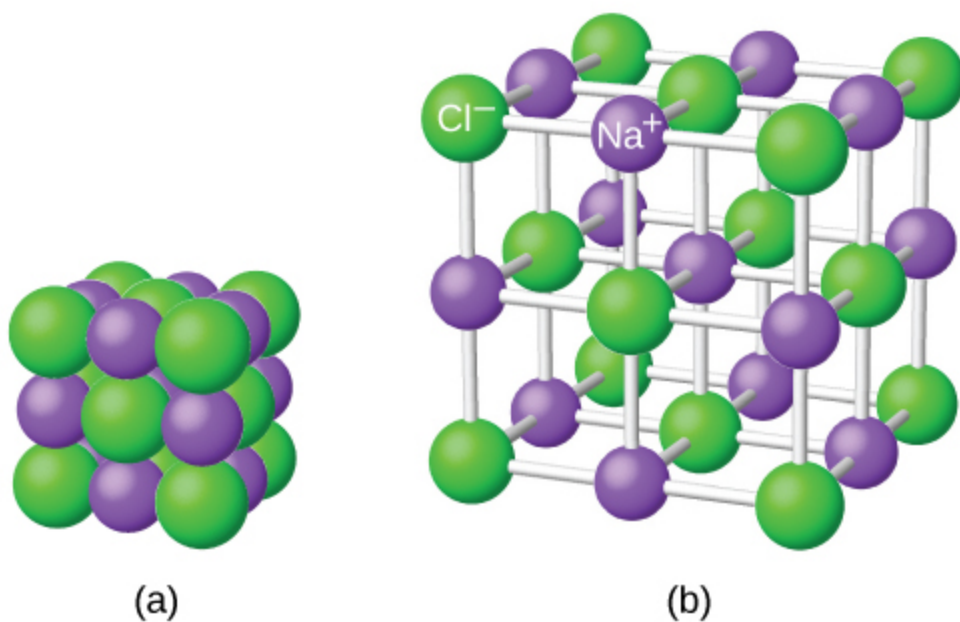
The Formation of Ionic Compounds

Binary ionic compounds are composed of just two elements: a metal (which forms the cations) and a nonmetal (which forms the anions). For example, NaCl is a binary ionic compound. We can think about the formation of such compounds in terms of the periodic properties of the elements. Many metallic elements have relatively low ionization potentials and lose electrons easily. These elements lie to the left in a period or near the bottom of a group on the periodic table. Nonmetal atoms have relatively high electron affinities and thus readily gain electrons lost by metal atoms, thereby filling their valence shells. Nonmetallic elements are found in the upper-right corner of the periodic table.

As all substances must be electrically neutral, the total number of positive charges on the cations of an ionic compound must equal the total number of negative charges on its anions. The formula of an ionic compound represents the simplest ratio of the numbers of ions necessary to give identical numbers of positive and negative charges. For example, the formula for aluminum oxide, Al_2O_3 , indicates that this ionic compound

contains two aluminum cations, Al^{3+} , for every three oxide anions, O^{2-} [thus, $(2 \times +3) + (3 \times -2) = 0$].

It is important to note, however, that the formula for an ionic compound does *not* represent the physical arrangement of its ions. It is incorrect to refer to a sodium chloride (NaCl) “molecule” because there is not a single ionic bond, *per se*, between any specific pair of sodium and chloride ions. The attractive forces between ions are isotropic—the same in all directions—meaning that any particular ion is equally attracted to all of the nearby ions of opposite charge. This results in the ions arranging themselves into a tightly bound, three-dimensional lattice structure. Sodium chloride, for example, consists of a regular arrangement of equal numbers of Na^+ cations and Cl^- anions ([\[link\]](#)).



The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is “bonded” to all of the surrounding ions—six in this case.

The strong electrostatic attraction between Na^+ and Cl^- ions holds them tightly together in solid NaCl. It requires 769 kJ of energy to dissociate one mole of solid NaCl into separate gaseous Na^+ and Cl^- ions:

Equation:



Electronic Structures of Cations

When forming a cation, an atom of a main group element tends to lose all of its valence electrons, thus assuming the electronic structure of the noble gas that precedes it in the periodic table. For groups 1 (the alkali metals) and 2 (the alkaline earth metals), the group numbers are equal to the numbers of valence shell electrons and, consequently, to the charges of the cations formed from atoms of these elements when all valence shell electrons are removed. For example, calcium is a group 2 element whose neutral atoms have 20 electrons and a ground state electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$. When a Ca atom loses both of its valence electrons, the result is a cation with 18 electrons, a 2+ charge, and an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6$. The Ca^{2+} ion is therefore isoelectronic with the noble gas Ar.

For groups 13–17, the group numbers exceed the number of valence electrons by 10 (accounting for the possibility of full *d* subshells in atoms of elements in the fourth and greater periods). Thus, the charge of a cation formed by the loss of all valence electrons is equal to the group number minus 10. For example, aluminum (in group 13) forms 3+ ions (Al^{3+}).

Exceptions to the expected behavior involve elements toward the bottom of the groups. In addition to the expected ions Tl^{3+} , Sn^{4+} , Pb^{4+} , and Bi^{5+} , a partial loss of these atoms' valence shell electrons can also lead to the formation of Tl^+ , Sn^{2+} , Pb^{2+} , and Bi^{3+} ions. The formation of these 1+, 2+, and 3+ cations is ascribed to the **inert pair effect**, which reflects the relatively low energy of the valence *s*-electron pair for atoms of the heavy

elements of groups 13, 14, and 15. Mercury (group 12) also exhibits an unexpected behavior: it forms a diatomic ion, Hg_2^{2+} (an ion formed from two mercury atoms, with an Hg-Hg bond), in addition to the expected monatomic ion Hg^{2+} (formed from only one mercury atom).

Transition and inner transition metal elements behave differently than main group elements. Most transition metal cations have $2+$ or $3+$ charges that result from the loss of their outermost s electron(s) first, sometimes followed by the loss of one or two d electrons from the next-to-outermost shell. For example, iron ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$) forms the ion Fe^{2+} ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$) by the loss of the $4s$ electron and the ion Fe^{3+} ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$) by the loss of the $4s$ electron and one of the $3d$ electrons. Although the d orbitals of the transition elements are—according to the Aufbau principle—the last to fill when building up electron configurations, the outermost s electrons are the first to be lost when these atoms ionize. When the inner transition metals form ions, they usually have a $3+$ charge, resulting from the loss of their outermost s electrons and a d or f electron.

Example:

Determining the Electronic Structures of Cations

There are at least 14 elements categorized as “essential trace elements” for the human body. They are called “essential” because they are required for healthy bodily functions, “trace” because they are required only in small amounts, and “elements” in spite of the fact that they are really ions. Two of these essential trace elements, chromium and zinc, are required as Cr^{3+} and Zn^{2+} . Write the electron configurations of these cations.

Solution

First, write the electron configuration for the neutral atoms:

Zn: $[\text{Ar}]3d^{10}4s^2$

Cr: $[\text{Ar}]3d^5 4s^1$

Next, remove electrons from the highest energy orbital. For the transition metals, electrons are removed from the s orbital first and then from the d orbital. For the p -block elements, electrons are removed from the p orbitals and then from the s orbital. Zinc is a member of group 12, so it should have

a charge of $2+$, and thus loses only the two electrons in its s orbital. Chromium is a transition element and should lose its s electrons and then its d electrons when forming a cation. Thus, we find the following electron configurations of the ions:



Check Your Learning

Potassium and magnesium are required in our diet. Write the electron configurations of the ions expected from these elements.

Note:

Answer:



Electronic Structures of Anions

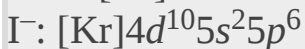
Most monatomic anions form when a neutral nonmetal atom gains enough electrons to completely fill its outer s and p orbitals, thereby reaching the electron configuration of the next noble gas. Thus, it is simple to determine the charge on such a negative ion: The charge is equal to the number of electrons that must be gained to fill the s and p orbitals of the parent atom. Oxygen, for example, has the electron configuration $1s^2 2s^2 2p^4$, whereas the oxygen anion has the electron configuration of the noble gas neon (Ne), $1s^2 2s^2 2p^6$. The two additional electrons required to fill the valence orbitals give the oxide ion the charge of $2-$ (O^{2-}).

Example:

Determining the Electronic Structure of Anions

Selenium and iodine are two essential trace elements that form anions. Write the electron configurations of the anions.

Solution

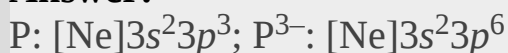


Check Your Learning

Write the electron configurations of a phosphorus atom and its negative ion. Give the charge on the anion.

Note:

Answer:



Key Concepts and Summary

Atoms gain or lose electrons to form ions with particularly stable electron configurations. The charges of cations formed by the representative metals may be determined readily because, with few exceptions, the electronic structures of these ions have either a noble gas configuration or a completely filled electron shell. The charges of anions formed by the nonmetals may also be readily determined because these ions form when nonmetal atoms gain enough electrons to fill their valence shells.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Does a cation gain protons to form a positive charge or does it lose electrons?

Solution:

The protons in the nucleus do not change during normal chemical reactions. Only the outer electrons move. Positive charges form when electrons are lost.

Exercise:**Problem:**

Iron(III) sulfate $[\text{Fe}_2(\text{SO}_4)_3]$ is composed of Fe^{3+} and SO_4^{2-} ions. Explain why a sample of iron(III) sulfate is uncharged.

Exercise:**Problem:**

Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: P, I, Mg, Cl, In, Cs, O, Pb, Co?

Solution:

P, I, Cl, and O would form anions because they are nonmetals. Mg, In, Cs, Pb, and Co would form cations because they are metals.

Exercise:**Problem:**

Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: Br, Ca, Na, N, F, Al, Sn, S, Cd?

Exercise:**Problem:**

Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:

(a) P

(b) Mg

(c) Al

(d) O

(e) Cl

(f) Cs

Solution:

(a) P^{3-} ; (b) Mg^{2+} ; (c) Al^{3+} ; (d) O^{2-} ; (e) Cl^- ; (f) Cs^+

Exercise:

Problem:

Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:

(a) I

(b) Sr

(c) K

(d) N

(e) S

(f) In

Exercise:

Problem:

Write the electron configuration for each of the following ions:

(a) As^{3-}

(b) I^-

(c) Be^{2+}

(d) Cd^{2+}

(e) O^{2-}

(f) Ga^{3+}

(g) Li^+

(h) N^{3-}

(i) Sn^{2+}

(j) Co^{2+}

(k) Fe^{2+}

(l) As^{3+}

Solution:

(a) $[\text{Ar}]4s^23d^{10}4p^6$; (b) $[\text{Kr}]4d^{10}5s^25p^6$ (c) $1s^2$ (d) $[\text{Kr}]4d^{10}$; (e) $[\text{He}]2s^22p^6$; (f) $[\text{Ar}]3d^{10}$; (g) $1s^2$ (h) $[\text{He}]2s^22p^6$ (i) $[\text{Kr}]4d^{10}5s^2$ (j) $[\text{Ar}]3d^7$ (k) $[\text{Ar}]3d^6$, (l) $[\text{Ar}]3d^{10}4s^2$

Exercise:

Problem:

Write the electron configuration for the monatomic ions formed from the following elements (which form the greatest concentration of monatomic ions in seawater):

(a) Cl

(b) Na

(c) Mg

(d) Ca

(e) K

(f) Br

(g) Sr

(h) F

Exercise:

Problem:

Write out the full electron configuration for each of the following atoms and for the monatomic ion found in binary ionic compounds containing the element:

(a) Al

(b) Br

(c) Sr

(d) Li

(e) As

(f) S

Solution:

(a) $1s^2 2s^2 2p^6 3s^2 3p^1$; Al^{3+} : $1s^2 2s^2 2p^6$; (b) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; (c) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$; Sr^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; (d) $1s^2 2s^1$; Li^+ : $1s^2$; (e) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; (f) $1s^2 2s^2 2p^6 3s^2 3p^4$; $1s^2 2s^2 2p^6 3s^2 3p^6$

Exercise:**Problem:**

From the labels of several commercial products, prepare a list of six ionic compounds in the products. For each compound, write the formula. (You may need to look up some formulas in a suitable reference.)

Glossary

inert pair effect

tendency of heavy atoms to form ions in which their valence s electrons are not lost

ionic bond

strong electrostatic force of attraction between cations and anions in an ionic compound

Covalent Bonding

By the end of this section, you will be able to:

- Describe the formation of covalent bonds
- Define electronegativity and assess the polarity of covalent bonds

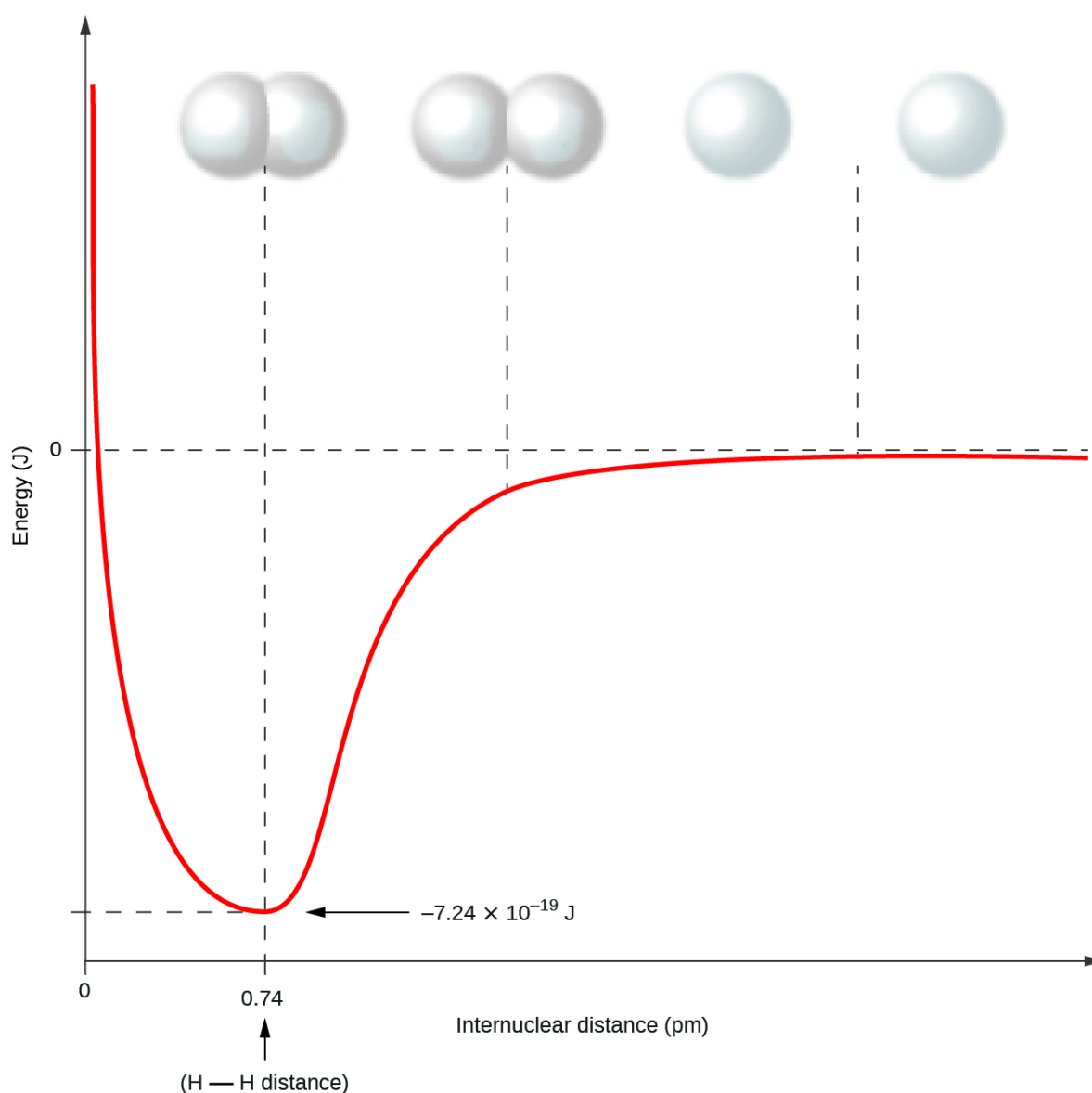
Ionic bonding results from the electrostatic attraction of oppositely charged ions that are typically produced by the transfer of electrons between metallic and nonmetallic atoms. A different type of bonding results from the mutual attraction of atoms for a “shared” pair of electrons. Such bonds are called **covalent bonds**. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an H_2 molecule; each hydrogen atom in the H_2 molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

Compounds that contain covalent bonds exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds are insoluble in water; since they are electrically neutral, they are poor conductors of electricity in any state.

Formation of Covalent Bonds

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. For example, the hydrogen molecule, H_2 , contains a covalent bond between its two hydrogen atoms. [\[link\]](#) illustrates why this bond is formed. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the x-axis is the distance between the two atoms. As the two atoms approach each other

(moving left along the x -axis), their valence orbitals ($1s$) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases. The **bond length** is determined by the distance at which the lowest potential energy is achieved.



The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.

It is essential to remember that energy must be added to break chemical bonds (an endothermic process), whereas forming chemical bonds releases energy (an exothermic process). In the case of H_2 , the covalent bond is very strong; a large amount of energy, 436 kJ, must be added to break the bonds in one mole of hydrogen molecules and cause the atoms to separate:

Equation:



Conversely, the same amount of energy is released when one mole of H_2 molecules forms from two moles of H atoms:

Equation:

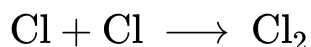


Pure vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in H_2 , Cl_2 , and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a **pure covalent bond**. Electrons shared in pure covalent bonds have an equal probability of being near each nucleus.

In the case of Cl_2 , each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:

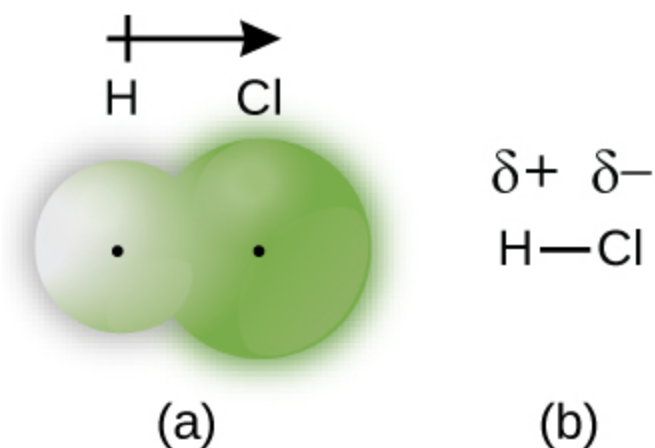
Equation:



The total number of electrons around each individual atom consists of six nonbonding electrons and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since the bonding atoms are identical, Cl_2 also features a pure covalent bond.

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a **polar covalent bond**, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge. [\[link\]](#) shows the distribution of electrons in the H–Cl bond. Note that the shaded area around Cl is much larger than it is around H. Compare this to [\[link\]](#), which shows the even distribution of electrons in the H_2 nonpolar bond.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter “delta,” δ , with a plus sign or minus sign to indicate whether the atom has a partial positive charge (δ^+) or a partial negative charge (δ^-). This symbolism is shown for the H–Cl molecule in [\[link\]](#).

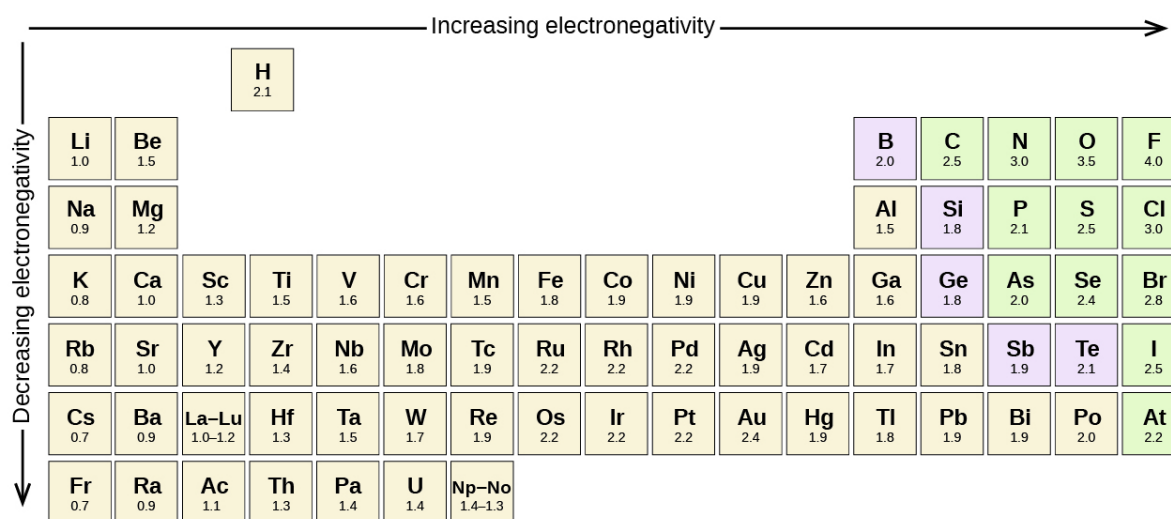


(a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols δ^+ and δ^- indicate the polarity of the H-Cl bond.

Electronegativity

Whether a bond is nonpolar or polar covalent is determined by a property of the bonding atoms called **electronegativity**. Electronegativity is a measure of the tendency of an atom to attract electrons (or electron density) towards itself. It determines how the shared electrons are distributed between the two atoms in a bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrons in a polar covalent bond are shifted toward the more electronegative atom; thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the larger the partial charges of the atoms.

[\[link\]](#) shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling ([\[link\]](#)). In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with others atoms since they have a full valence shell. (While noble gas compounds such as XeO₂ do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)



The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table.

Electronegativity versus Electron Affinity

We must be careful not to confuse electronegativity and electron affinity. The electron affinity of an element is a measurable physical quantity, namely, the energy released or absorbed when an isolated gas-phase atom acquires an electron, measured in kJ/mol. Electronegativity, on the other hand, describes how tightly an atom attracts electrons in a bond. It is a dimensionless quantity that is calculated, not measured. Pauling derived the first electronegativity values by comparing the amounts of energy required to break different types of bonds. He chose an arbitrary relative scale ranging from 0 to 4.

Note:

Linus Pauling

Linus Pauling, shown in [\[link\]](#), is the only person to have received two unshared (individual) Nobel Prizes: one for chemistry in 1954 for his work on the nature of chemical bonds and one for peace in 1962 for his opposition to weapons of mass destruction. He developed many of the theories and concepts that are foundational to our current understanding of chemistry, including electronegativity and resonance structures.

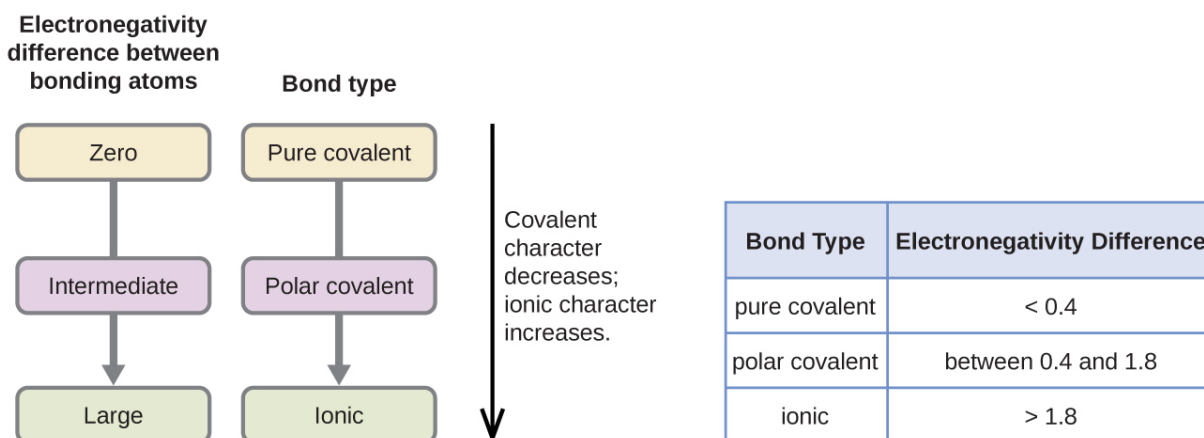


Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.

Pauling also contributed to many other fields besides chemistry. His research on sickle cell anemia revealed the cause of the disease—the presence of a genetically inherited abnormal protein in the blood—and paved the way for the field of molecular genetics. His work was also pivotal in curbing the testing of nuclear weapons; he proved that radioactive fallout from nuclear testing posed a public health risk.

Electronegativity and Bond Type

The absolute value of the difference in electronegativity (ΔEN) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). [\[link\]](#) shows the relationship between electronegativity difference and bond type.



As the electronegativity difference increases between two atoms, the bond becomes more ionic.

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in [\[link\]](#). This table is just a general guide, however, with many exceptions. For example, the H and F atoms in HF have an electronegativity difference of 1.9, and the N and H atoms in NH_3 a difference of 0.9, yet both of these compounds form bonds that are considered polar covalent. Likewise, the Na and Cl atoms in NaCl have an electronegativity difference of 2.1, and the Mn and I atoms in MnI_2 have a difference of 1.0, yet both of these substances form ionic compounds.

The best guide to the covalent or ionic character of a bond is to consider the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are generally covalent; bonding between a metal and a nonmetal is often ionic.

Some compounds contain both covalent and ionic bonds. The atoms in polyatomic ions, such as OH^- , NO_3^- , and NH_4^+ , are held together by polar covalent bonds. However, these polyatomic ions form ionic compounds by combining with ions of opposite charge. For example, potassium nitrate, KNO_3 , contains the K^+ cation and the polyatomic NO_3^- anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic

attraction between the ions K^+ and NO_3^- , as well as covalent between the nitrogen and oxygen atoms in NO_3^- .

Example:

Electronegativity and Bond Polarity

Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in [\[link\]](#), arrange the following covalent bonds—all commonly found in amino acids—in order of increasing polarity. Then designate the positive and negative atoms using the symbols δ^+ and δ^- :

C–H, C–N, C–O, N–H, O–H, S–H

Solution

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the δ^- designation is the more electronegative of the two. [\[link\]](#) shows these bonds in order of increasing polarity.

Bond Polarity and Electronegativity Difference

Bond	ΔEN	Polarity
C–H	0.4	$\overset{\delta^-}{\text{C}} - \overset{\delta^+}{\text{H}}$
S–H	0.4	$\overset{\delta^-}{\text{S}} - \overset{\delta^+}{\text{H}}$
C–N	0.5	$\overset{\delta^+}{\text{C}} - \overset{\delta^-}{\text{N}}$
N–H	0.9	$\overset{\delta^-}{\text{N}} - \overset{\delta^+}{\text{H}}$

Bond Polarity and Electronegativity Difference

Bond	ΔEN	Polarity
C–O	1.0	$\overset{\delta+}{\text{C}}-\overset{\delta-}{\text{O}}$
O–H	1.4	$\overset{\delta-}{\text{O}}-\overset{\delta+}{\text{H}}$

Check Your Learning

Silicones are polymeric compounds containing, among others, the following types of covalent bonds: Si–O, Si–C, C–H, and C–C. Using the electronegativity values in [\[link\]](#), arrange the bonds in order of increasing polarity and designate the positive and negative atoms using the symbols $\delta+$ and $\delta-$.

Note:

Answer:

Bond	Electronegativity Difference	Polarity
C–C	0.0	nonpolar
C–H	0.4	$\overset{\delta-}{\text{C}}-\overset{\delta+}{\text{H}}$
Si–C	0.7	$\overset{\delta+}{\text{Si}}-\overset{\delta-}{\text{C}}$

Bond	Electronegativity Difference	Polarity
Si–O	1.7	$\delta^+ \delta^-$ Si–O

Key Concepts and Summary

Covalent bonds form when electrons are shared between atoms and are attracted by the nuclei of both atoms. In pure covalent bonds, the electrons are shared equally. In polar covalent bonds, the electrons are shared unequally, as one atom exerts a stronger force of attraction on the electrons than the other. The ability of an atom to attract a pair of electrons in a chemical bond is called its electronegativity. The difference in electronegativity between two atoms determines how polar a bond will be. In a diatomic molecule with two identical atoms, there is no difference in electronegativity, so the bond is nonpolar or pure covalent. When the electronegativity difference is very large, as is the case between metals and nonmetals, the bonding is characterized as ionic.

Chemistry End of Chapter Exercises

Exercise:

Problem: Why is it incorrect to speak of a molecule of solid NaCl?

Solution:

NaCl consists of discrete ions arranged in a crystal lattice, not covalently bonded molecules.

Exercise:

Problem:

What information can you use to predict whether a bond between two atoms is covalent or ionic?

Exercise:**Problem:**

Predict which of the following compounds are ionic and which are covalent, based on the location of their constituent atoms in the periodic table:

(a) Cl_2CO

(b) MnO

(c) NCl_3

(d) CoBr_2

(e) K_2S

(f) CO

(g) CaF_2

(h) HI

(i) CaO

(j) IBr

(k) CO_2

Solution:

ionic: (b), (d), (e), (g), and (i); covalent: (a), (c), (f), (h), (j), and (k)

Exercise:

Problem:

Explain the difference between a nonpolar covalent bond, a polar covalent bond, and an ionic bond.

Exercise:**Problem:**

From its position in the periodic table, determine which atom in each pair is more electronegative:

- (a) Br or Cl
 - (b) N or O
 - (c) S or O
 - (d) P or S
 - (e) Si or N
 - (f) Ba or P
 - (g) N or K
-

Solution:

(a) Cl; (b) O; (c) O; (d) S; (e) N; (f) P; (g) N

Exercise:**Problem:**

From its position in the periodic table, determine which atom in each pair is more electronegative:

- (a) N or P
- (b) N or Ge

- (c) S or F
- (d) Cl or S
- (e) H or C
- (f) Se or P
- (g) C or Si

Exercise:

Problem:

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

- (a) C, F, H, N, O
- (b) Br, Cl, F, H, I
- (c) F, H, O, P, S
- (d) Al, H, Na, O, P
- (e) Ba, H, N, O, As

Solution:

(a) H, C, N, O, F; (b) H, I, Br, Cl, F; (c) H, P, S, O, F; (d) Na, Al, H, P, O; (e) Ba, H, As, N, O

Exercise:

Problem:

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

- (a) As, H, N, P, Sb

(b) Cl, H, P, S, Si

(c) Br, Cl, Ge, H, Sr

(d) Ca, H, K, N, Si

(e) Cl, Cs, Ge, H, Sr

Exercise:

Problem:

Which atoms can bond to sulfur so as to produce a positive partial charge on the sulfur atom?

Solution:

N, O, F, and Cl

Exercise:

Problem: Which is the most polar bond?

(a) C–C

(b) C–H

(c) N–H

(d) O–H

(e) Se–H

Exercise:

Problem:

Identify the more polar bond in each of the following pairs of bonds:

(a) HF or HCl

(b) NO or CO

(c) SH or OH

(d) PCl or SCl

(e) CH or NH

(f) SO or PO

(g) CN or NN

Solution:

(a) HF; (b) CO; (c) OH; (d) PCl; (e) NH; (f) PO; (g) CN

Exercise:

Problem:

Which of the following molecules or ions contain polar bonds?

(a) O₃

(b) S₈

(c) O₂²⁻

(d) NO₃⁻

(e) CO₂

(f) H₂S

(g) BH₄⁻

Glossary

bond length

distance between the nuclei of two bonded atoms at which the lowest potential energy is achieved

covalent bond

bond formed when electrons are shared between atoms

electronegativity

tendency of an atom to attract electrons in a bond to itself

polar covalent bond

covalent bond between atoms of different electronegativities; a covalent bond with a positive end and a negative end

pure covalent bond

(also, nonpolar covalent bond) covalent bond between atoms of identical electronegativities

Lewis Symbols and Structures

By the end of this section, you will be able to:

- Write Lewis symbols for neutral atoms and ions
- Draw Lewis structures depicting the bonding in simple molecules

Thus far in this chapter, we have discussed the various types of bonds that form between atoms and/or ions. In all cases, these bonds involve the sharing or transfer of valence shell electrons between atoms. In this section, we will explore the typical method for depicting valence shell electrons and chemical bonds, namely Lewis symbols and Lewis structures.

Lewis Symbols

We use Lewis symbols to describe valence electron configurations of atoms and monatomic ions. A **Lewis symbol** consists of an elemental symbol surrounded by one dot for each of its valence electrons:

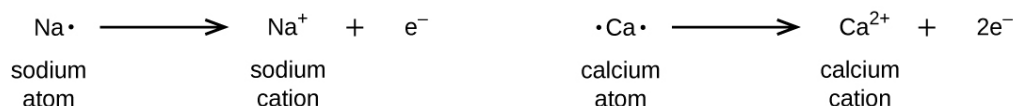


[\[link\]](#) shows the Lewis symbols for the elements of the third period of the periodic table.

Atoms	Electronic Configuration	Lewis Symbol
sodium	$[\text{Ne}]3s^1$	$\text{Na}\cdot$
magnesium	$[\text{Ne}]3s^2$	$\cdot\text{Mg}\cdot$
aluminum	$[\text{Ne}]3s^23p^1$	$\cdot\overset{\cdot}{\underset{\cdot}{\text{Al}}}\cdot$
silicon	$[\text{Ne}]3s^23p^2$	$\cdot\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{Si}}}}\cdot$
phosphorus	$[\text{Ne}]3s^23p^3$	$\cdot\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{P}}}}}\cdot$
sulfur	$[\text{Ne}]3s^23p^4$	$\cdot\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{S}}}}}}\cdot$
chlorine	$[\text{Ne}]3s^23p^5$	$\cdot\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{Cl}}}}}}}\cdot$
argon	$[\text{Ne}]3s^23p^6$	$\cdot\overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{Ar}}}}}}}}\cdot$

Lewis symbols illustrating the number of valence electrons for each element in the third period of the periodic table.

Lewis symbols can also be used to illustrate the formation of cations from atoms, as shown here for sodium and calcium:



Likewise, they can be used to show the formation of anions from atoms, as shown here for chlorine and sulfur:



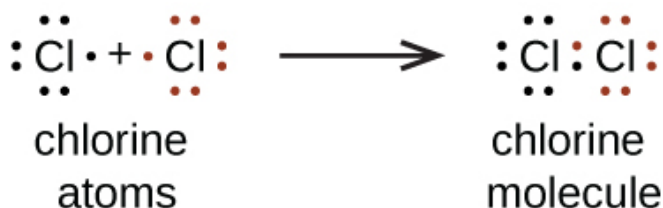
[\[link\]](#) demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

Metal		Nonmetal		Ionic Compound
$\text{Na} \cdot$ sodium atom	+	$\cdot \ddot{\text{Cl}} \cdot$ chlorine atom	\longrightarrow	$\text{Na}^+ \left[\cdot \ddot{\text{Cl}} \cdot \right]^-$ sodium chloride (sodium ion and chloride ion)
$\cdot \text{Mg} \cdot$ magnesium atom	+	$\cdot \ddot{\text{O}} \cdot$ oxygen atom	\longrightarrow	$\text{Mg}^{2+} \left[\cdot \ddot{\text{O}} \cdot \right]^{2-}$ magnesium oxide (magnesium ion and oxide ion)
$\cdot \text{Ca} \cdot$ calcium atom	+	$2 \cdot \ddot{\text{F}} \cdot$ fluorine atoms	\longrightarrow	$\text{Ca}^{2+} \left[\cdot \ddot{\text{F}} \cdot \right]_2^-$ calcium fluoride (calcium ion and two fluoride ions)

Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.

Lewis Structures

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in **Lewis structures**, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:



The Lewis structure indicates that each Cl atom has three pairs of electrons that are not used in bonding (called **lone pairs**) and one shared pair of electrons (written between the atoms). A dash (or line) is sometimes used to indicate a shared pair of electrons:



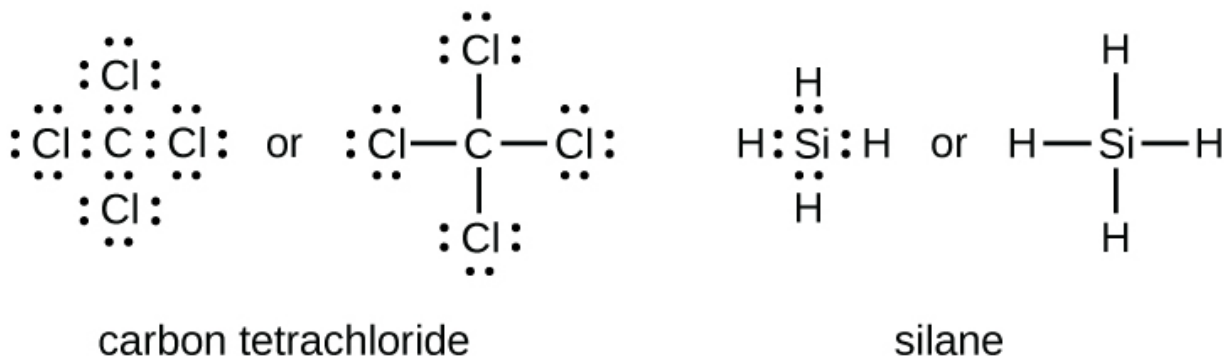
A single shared pair of electrons is called a **single bond**. Each Cl atom interacts with eight valence electrons: the six in the lone pairs and the two in the single bond.

The Octet Rule

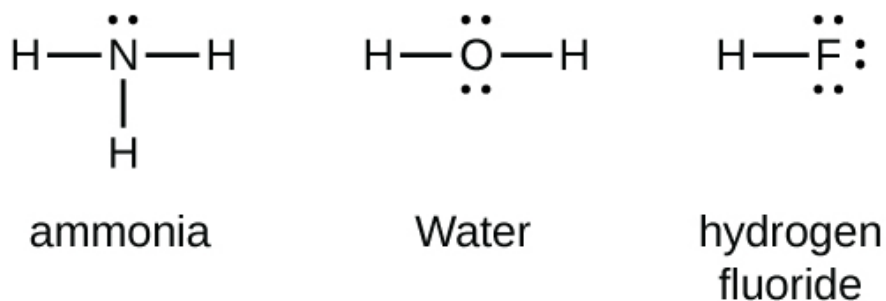
The other halogen molecules (F_2 , Br_2 , I_2 , and At_2) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the **octet rule**.

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons

to fill its valence shell, it is an exception to the octet rule. The transition elements and inner transition elements also do not follow the octet rule:

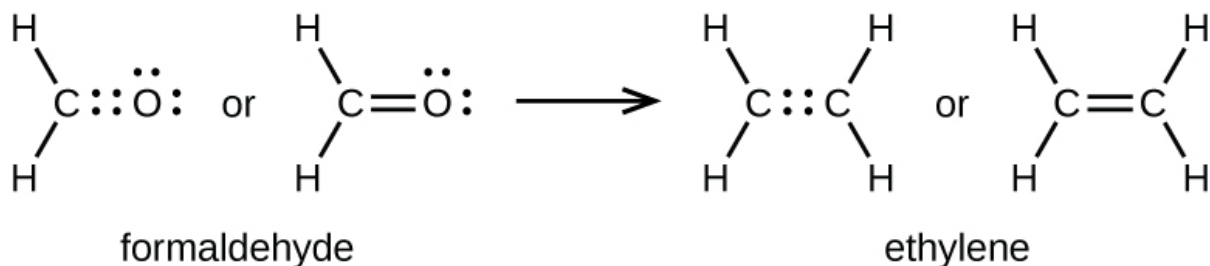


Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:

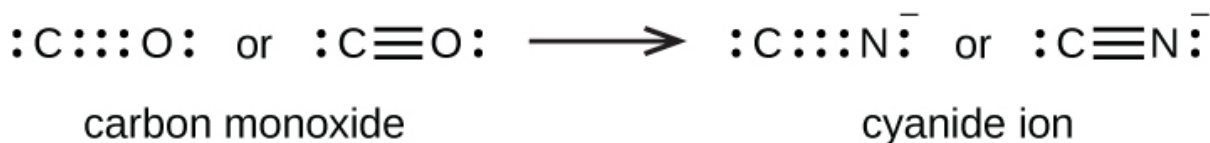


Double and Triple Bonds

As previously mentioned, when a pair of atoms shares one pair of electrons, we call this a single bond. However, a pair of atoms may need to share more than one pair of electrons in order to achieve the requisite octet. A **double bond** forms when two pairs of electrons are shared between a pair of atoms, as between the carbon and oxygen atoms in CH_2O (formaldehyde) and between the two carbon atoms in C_2H_4 (ethylene):

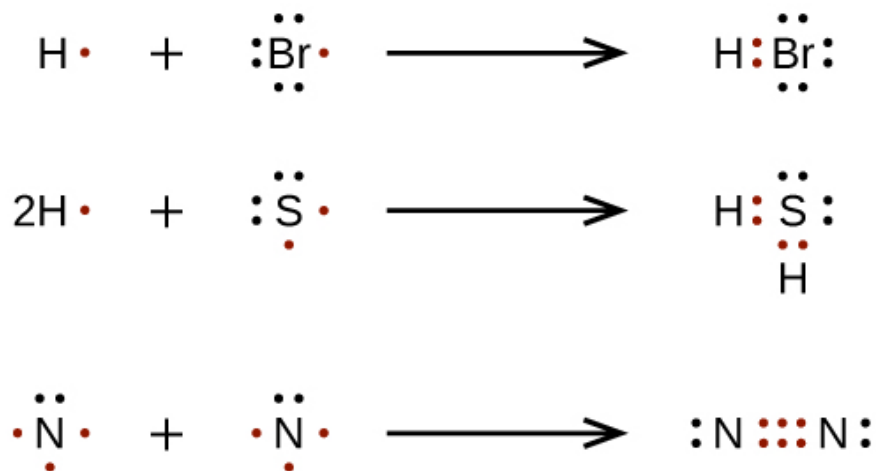


A **triple bond** forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion (CN⁻):



Writing Lewis Structures with the Octet Rule

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:



For more complicated molecules and molecular ions, it is helpful to follow the step-by-step procedure outlined here:

1. Determine the total number of valence (outer shell) electrons. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the

center.) Connect each atom to the central atom with a single bond (one electron pair).

3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of SiH_4 , CHO_2^- , NO^+ , and OF_2 as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion.

- For a molecule, we add the number of valence electrons on each atom in the molecule:

Equation:

$$\begin{aligned} &\text{SiH}_4 \\ &\text{Si: } 4 \text{ valence electrons/atom} \times 1 \text{ atom} = 4 \\ &+ \text{H: } 1 \text{ valence electron/atom} \times 4 \text{ atoms} = 4 \\ & \\ &= 8 \text{ valence electrons} \end{aligned}$$

- For a *negative ion*, such as CHO_2^- , we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):

Equation:

$$\begin{aligned} &\text{CHO}_2^- \\ &\text{C: } 4 \text{ valence electrons/atom} \times 1 \text{ atom} = 4 \\ &\text{H: } 1 \text{ valence electron/atom} \times 1 \text{ atom} = 1 \\ &\text{O: } 6 \text{ valence electrons/atom} \times 2 \text{ atoms} = 12 \\ &+ \qquad \qquad \qquad 1 \text{ additional electron} = 1 \\ & \\ &= 18 \text{ valence electrons} \end{aligned}$$

- For a *positive ion*, such as NO^+ , we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

Equation:



$$\text{N: } 5 \text{ valence electrons/atom} \times 1 \text{ atom} = 5$$

$$\text{O: } 6 \text{ valence electron/atom} \times 1 \text{ atom} = 6$$

$$+ -1 \text{ electron (positive charge)} = -1$$

$$= 10 \text{ valence electrons}$$

- Since OF_2 is a neutral molecule, we simply add the number of valence electrons:

Equation:

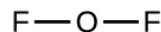
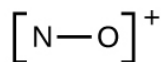
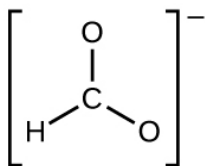
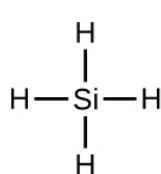


$$\text{O: } 6 \text{ valence electrons/atom} \times 1 \text{ atom} = 6$$

$$+ \text{F: } 7 \text{ valence electrons/atom} \times 2 \text{ atoms} = 14$$

$$= 20 \text{ valence electrons}$$

- Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)

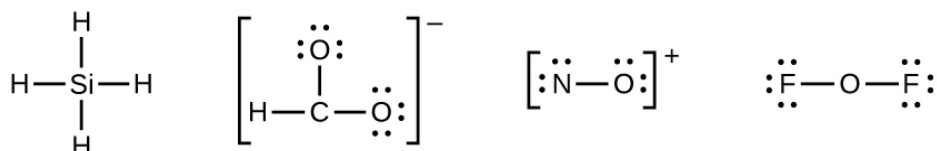


When several arrangements of atoms are possible, as for CHO_2^- , we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In CHO_2^- , the less

electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in POCl_3 , S in SO_2 , and Cl in ClO_4^- . An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.

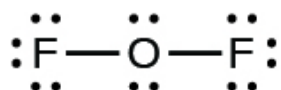
- Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.

- There are no remaining electrons on SiH_4 , so it is unchanged:



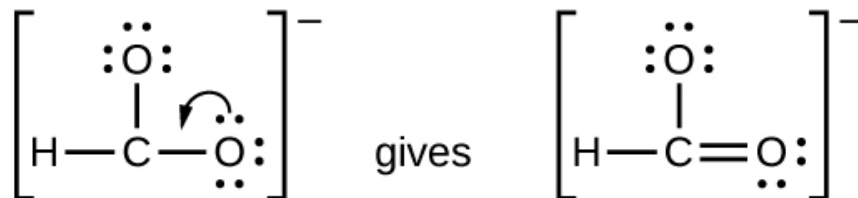
- Place all remaining electrons on the central atom.

- For SiH_4 , CHO_2^- , and NO^+ , there are no remaining electrons; we already placed all of the electrons determined in Step 1.
- For OF_2 , we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:

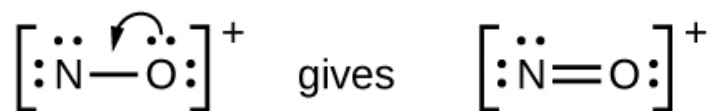


- Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

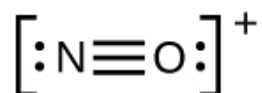
- SiH_4 : Si already has an octet, so nothing needs to be done.
- CHO_2^- : We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:



- NO^+ : For this ion, we added eight valence electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:



This still does not produce an octet, so we must move another pair, forming a triple bond:



- In OF_2 , each atom has an octet as drawn, so nothing changes.

Example:

Writing Lewis Structures

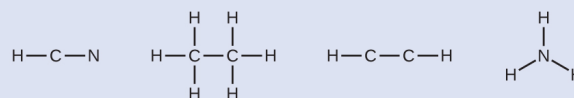
NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

Solution

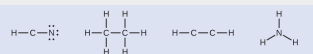
Calculate the number of valence electrons.

HCN:	$\times 1) \times 1) \times 1)$	H_3CCH_3 :	$\times 3) \times 4) \times 3)$	HCCH :	$\times 1) \times 4) \times 1)$	NH_3 :	$\times 1) \times 1)$
(1	+ + =	(1	+ + =	(1	+ + =	(5	+ =
4	5 10	2	1 14	2	1 10	3	8

Draw a skeleton and connect the atoms with single bonds. Remember that H is never a central atom:

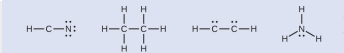
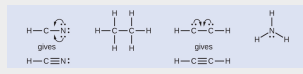


Where needed, distribute electrons to the terminal atoms:



HCN:	H_3CCH_3 : no	HCCH : no	NH_3 : no
six	electron	terminal	terminal
electrons	remain	atoms	atoms
placed		capable of	capable
on N		accepting	of
		electrons	accepting
			electrons

HCN:	H_3CCH_3 : no	HCCH :	NH_3 : two
------	-------------------------------	-----------------	---------------------

needed, place remaining electrons on the central atom:		no electrons remain	electrons remain	four electrons placed on carbon	electrons placed on nitrogen
Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:	HCN: H ₃ CCH ₃ : all form two more C–N bonds	all atoms have the correct number of electrons	HCCH: form a triple bond between the two carbon atoms	NH ₃ : all atoms have the correct number of electrons	

Check Your Learning

Both carbon monoxide, CO, and carbon dioxide, CO₂, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO₂ has been implicated in global climate change. What are the Lewis structures of these two molecules?

Note:

Answer:

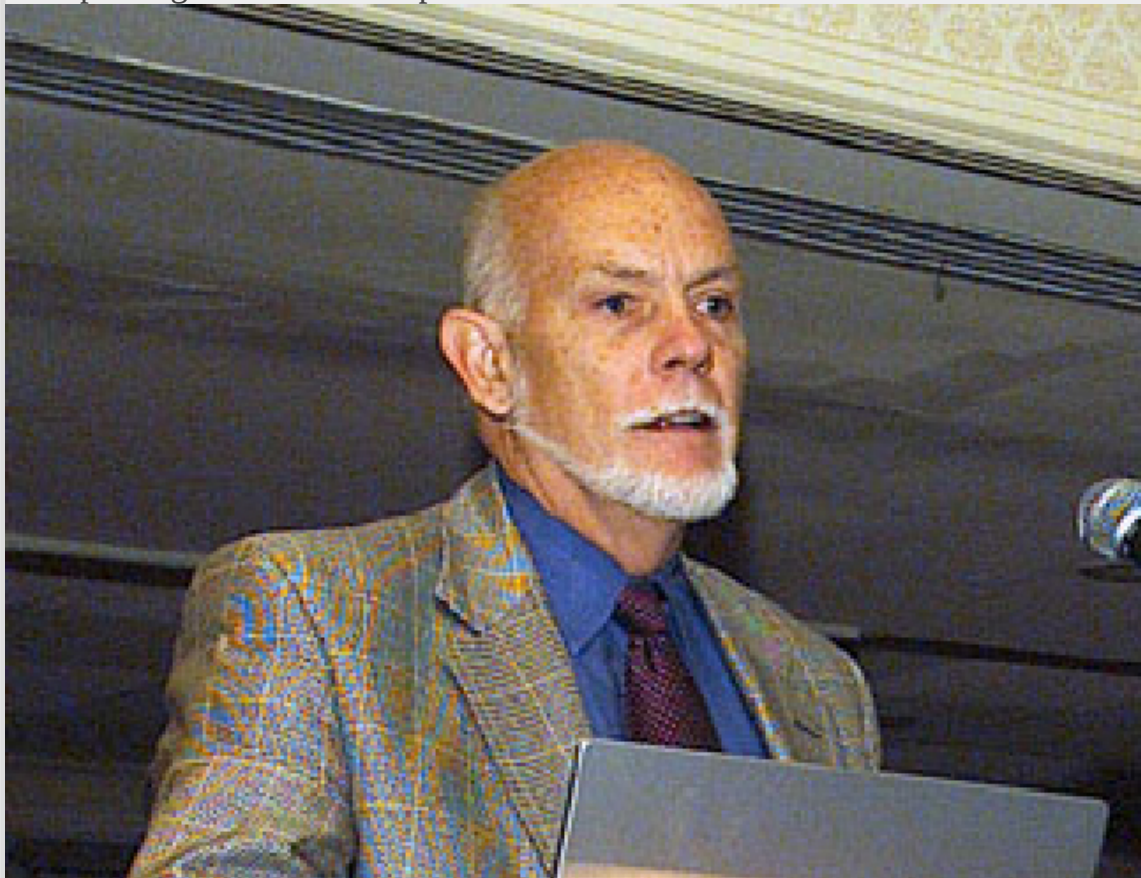


Note:

Fullerene Chemistry

Carbon soot has been known to man since prehistoric times, but it was not until fairly recently that the molecular structure of the main component of soot was discovered. In 1996, the Nobel Prize in Chemistry was awarded to Richard Smalley ([link](#)), Robert Curl, and Harold Kroto for their work in discovering a new form of carbon, the C₆₀ buckminsterfullerene molecule ([link](#)). An entire class of compounds, including spheres and tubes of various shapes, were discovered based on C₆₀. This

type of molecule, called a fullerene, shows promise in a variety of applications. Because of their size and shape, fullerenes can encapsulate other molecules, so they have shown potential in various applications from hydrogen storage to targeted drug delivery systems. They also possess unique electronic and optical properties that have been put to good use in solar powered devices and chemical sensors.



Richard Smalley (1943–2005), a professor of physics, chemistry, and astronomy at Rice University, was one of the leading advocates for fullerene chemistry. Upon his death in 2005, the US Senate honored him as the “Father of Nanotechnology.” (credit: United States Department of Energy)

Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

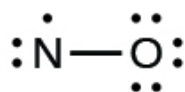
- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

Odd-electron Molecules

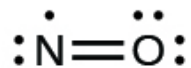
We call molecules that contain an odd number of electrons **free radicals**. Nitric oxide, NO, is an example of an odd-electron molecule; it is produced in internal combustion engines when oxygen and nitrogen react at high temperatures.

To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

1. *Determine the total number of valence (outer shell) electrons.* The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
2. *Draw a skeleton structure of the molecule.* We can easily draw a skeleton with an N–O single bond:
N–O
3. *Distribute the remaining electrons as lone pairs on the terminal atoms.* In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus oxygen has the filled valence shell:

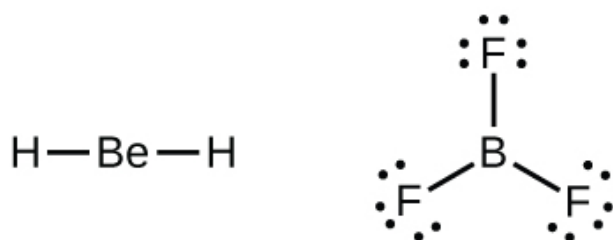


4. *Place all remaining electrons on the central atom.* Since there are no remaining electrons, this step does not apply.
5. *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible.* We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond. (We cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons:)

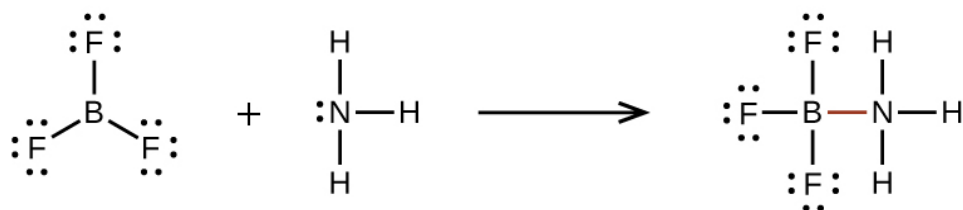


Electron-deficient Molecules

We will also encounter a few molecules that contain central atoms that do not have a filled valence shell. Generally, these are molecules with central atoms from groups 2 and 13, outer atoms that are hydrogen, or other atoms that do not form multiple bonds. For example, in the Lewis structures of beryllium dihydride, BeH_2 , and boron trifluoride, BF_3 , the beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in BF_3 , satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron deficient boron. The reactivity of the compound is also consistent with an electron deficient boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.

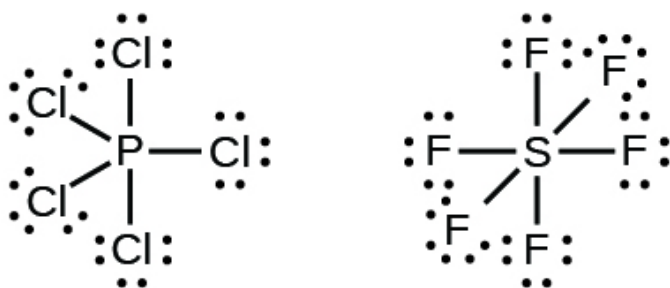


An atom like the boron atom in BF_3 , which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example, NH_3 reacts with BF_3 because the lone pair on nitrogen can be shared with the boron atom:



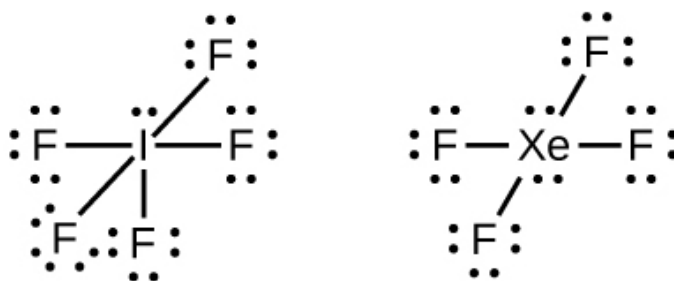
Hypervalent Molecules

Elements in the second period of the periodic table ($n = 2$) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one $2s$ and three $2p$ orbitals). Elements in the third and higher periods ($n \geq 3$) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty d orbitals in the same shell. Molecules formed from these elements are sometimes called **hypervalent molecules**. [\[link\]](#) shows the Lewis structures for two hypervalent molecules, PCl_5 and SF_6 .



In PCl_5 , the central atom phosphorus shares five pairs of electrons. In SF_6 , sulfur shares six pairs of electrons.

In some hypervalent molecules, such as IF_5 and XeF_4 , some of the electrons in the outer shell of the central atom are lone pairs:



When we write the Lewis structures for these molecules, we find that we have electrons left over after filling the valence shells of the outer atoms with eight electrons. These additional electrons must be assigned to the central atom.

Example:

Writing Lewis Structures: Octet Rule Violations

Xenon is a noble gas, but it forms a number of stable compounds. We examined XeF_4 earlier. What are the Lewis structures of XeF_2 and XeF_6 ?

Solution

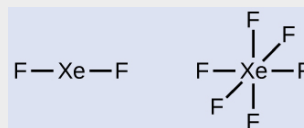
We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

Calculate the number of valence electrons:

$$\begin{array}{l} \text{XeF}_2: 8 + \quad \times 7 = \\ \quad \quad (2) \quad \quad 22 \end{array} \qquad \begin{array}{l} \text{XeF}_6: 8 + \quad \times 7 = \\ \quad \quad (6) \quad \quad 50 \end{array}$$

Draw a skeleton joining the atoms by single bonds.

Xenon will be the central atom because fluorine cannot be a central atom:



Distribute the remaining electrons.

XeF_2 : We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms have empty valence shell

d orbitals and 2 shows can accommodate more than eight electrons. The Lewis structure of XeF_6 shows two bonding pairs and three lone pairs of electrons around the Xe atom:

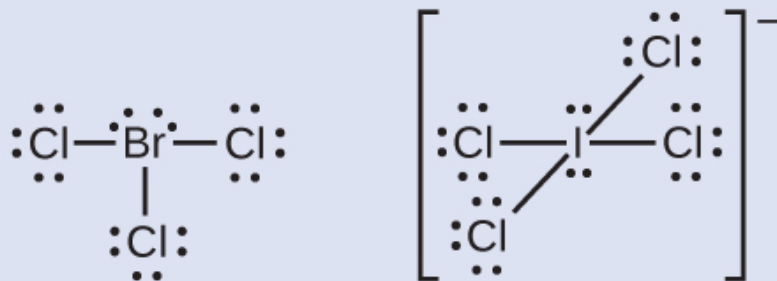
XeF_6 : We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:

Check Your Learning

The halogens form a class of compounds called the interhalogens, in which halogen atoms covalently bond to each other. Write the Lewis structures for the interhalogens BrCl_3 and ICl_4^- .

Note:

Answer:



Key Concepts and Summary

Valence electronic structures can be visualized by drawing Lewis symbols (for atoms and monatomic ions) and Lewis structures (for molecules and polyatomic ions). Lone pairs, unpaired electrons, and single, double, or triple bonds are used to indicate where the valence electrons are located around each atom in a Lewis structure. Most structures—especially those containing second row elements—obey the octet rule, in which every atom (except H) is surrounded by eight electrons. Exceptions to the octet rule occur for odd-electron molecules (free radicals), electron-deficient molecules, and hypervalent molecules.

Chemistry End of Chapter Exercises

Exercise:

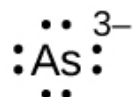
Problem: Write the Lewis symbols for each of the following ions:



(g) N^{3-}

Solution:

(a) eight electrons:



;

(b) eight electrons:

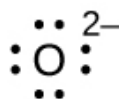


;

(c) no electrons

 $\text{Be}^{2+};$

(d) eight electrons:



;

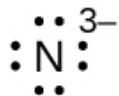
(e) no electrons

 Ga^{3+} ;

(f) no electrons

 Li^+ ;

(g) eight electrons:



Exercise:

Problem:

Many monatomic ions are found in seawater, including the ions formed from the following list of elements. Write the Lewis symbols for the monatomic ions formed from the following elements:

(a) Cl

(b) Na

(c) Mg

(d) Ca

(e) K

(f) Br

(g) Sr

(h) F

Exercise:

Problem:

Write the Lewis symbols of the ions in each of the following ionic compounds and the Lewis symbols of the atom from which they are formed:

(a) MgS

(b) Al₂O₃

(c) GaCl₃

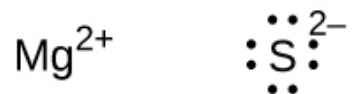
(d) K₂O

(e) Li₃N

(f) KF

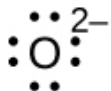
Solution:

(a)

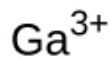


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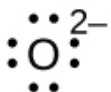
(b)



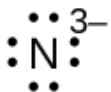
;
(c)



;
(d)



;
(e)



;
(f)

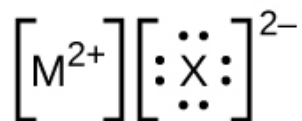


Exercise:

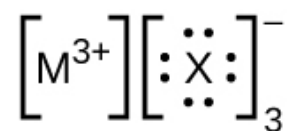
Problem:

In the Lewis structures listed here, M and X represent various elements in the third period of the periodic table. Write the formula of each compound using the chemical symbols of each element:

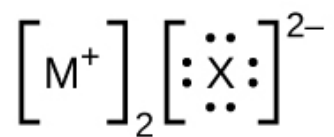
(a)



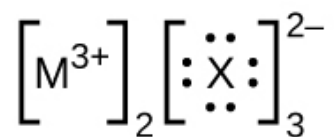
(b)



(c)



(d)



Exercise:

Problem:

Write the Lewis structure for the diatomic molecule P_2 , an unstable form of phosphorus found in high-temperature phosphorus vapor.

Solution:



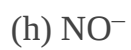
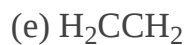
Exercise:

Problem: Write Lewis structures for the following:

(a) H_2

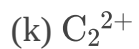
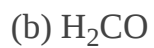
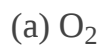
(b) HBr

(c) PCl_3



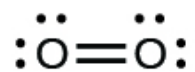
Exercise:

Problem: Write Lewis structures for the following:



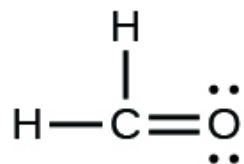
Solution:





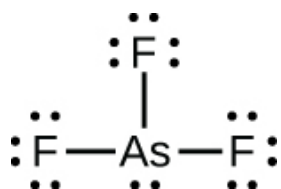
In this case, the Lewis structure is inadequate to depict the fact that experimental studies have shown two unpaired electrons in each oxygen molecule.

(b)



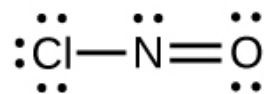
;

(c)



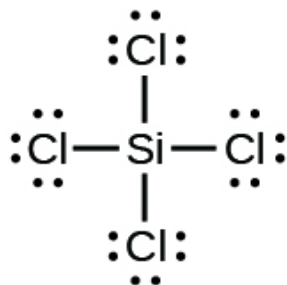
;

(d)



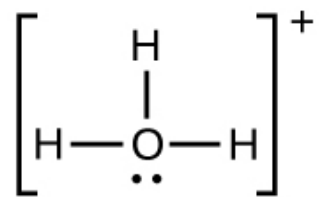
;

(e)

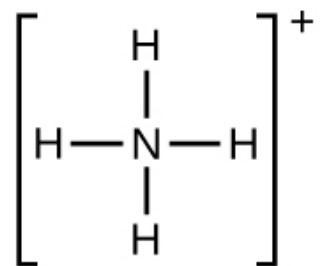


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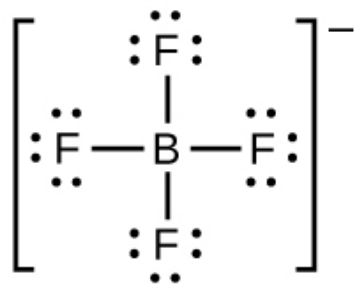
(f)



;
(g)



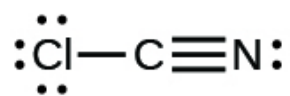
;
(h)



;
(i)



;
(j)



;
(k)



Exercise:

Problem: Write Lewis structures for the following:

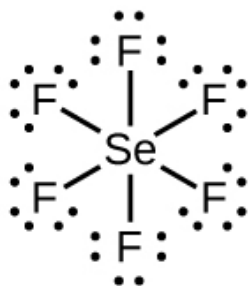


Exercise:

Problem: Write Lewis structures for the following:

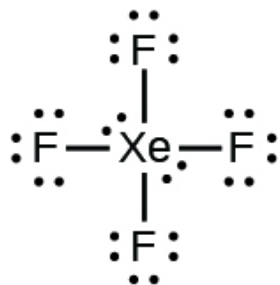


Solution:



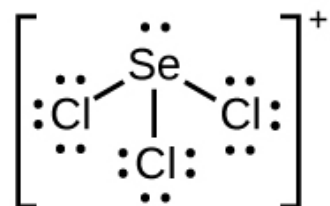
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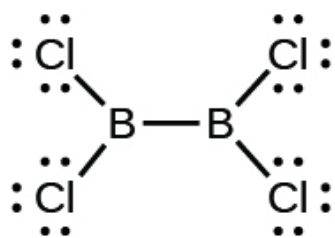
;

(c) SeCl_3^+ :



;

(d) Cl_2BBCl_2 :



Exercise:

Problem: Write Lewis structures for:

(a) PO_4^{3-}

(b) ICl_4^-

(c) SO_3^{2-}

(d) HONO

Exercise:

Problem:

Correct the following statement: “The bonds in solid PbCl_2 are ionic; the bond in a HCl molecule is covalent. Thus, all of the valence electrons in PbCl_2 are located on the Cl^- ions, and all of the valence electrons in a HCl molecule are shared between the H and Cl atoms.”

Solution:

Two valence electrons per Pb atom are transferred to Cl atoms; the resulting Pb^{2+} ion has a $6s^2$ valence shell configuration. Two of the valence electrons in the HCl molecule are shared, and the other six are located on the Cl atom as lone pairs of electrons.

Exercise:

Problem: Write Lewis structures for the following molecules or ions:

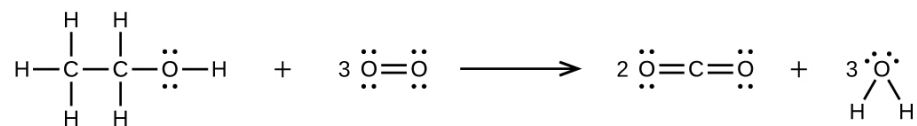
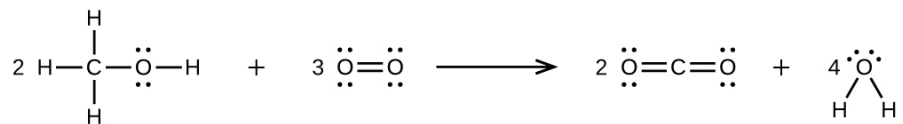
(a) SbH_3

(b) XeF_2

(c) Se_8 (a cyclic molecule with a ring of eight Se atoms)

Exercise:**Problem:**

Methanol, H_3COH , is used as the fuel in some race cars. Ethanol, $\text{C}_2\text{H}_5\text{OH}$, is used extensively as motor fuel in Brazil. Both methanol and ethanol produce CO_2 and H_2O when they burn. Write the chemical equations for these combustion reactions using Lewis structures instead of chemical formulas.

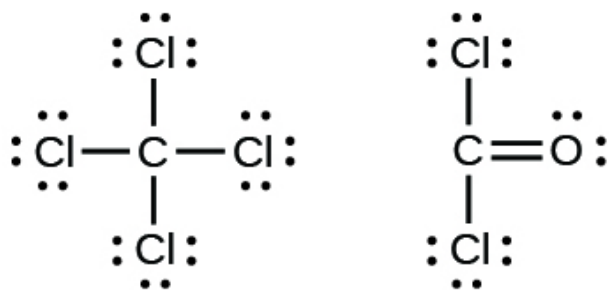
Solution:

Exercise:**Problem:**

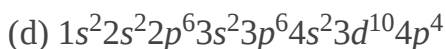
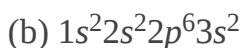
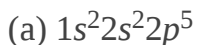
Many planets in our solar system contain organic chemicals including methane (CH_4) and traces of ethylene (C_2H_4), ethane (C_2H_6), propyne (H_3CCCH), and diacetylene (HCCCCCH). Write the Lewis structures for each of these molecules.

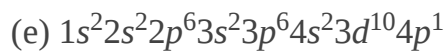
Exercise:**Problem:**

Carbon tetrachloride was formerly used in fire extinguishers for electrical fires. It is no longer used for this purpose because of the formation of the toxic gas phosgene, Cl_2CO . Write the Lewis structures for carbon tetrachloride and phosgene.

Solution:**Exercise:****Problem:**

Identify the atoms that correspond to each of the following electron configurations. Then, write the Lewis symbol for the common ion formed from each atom:



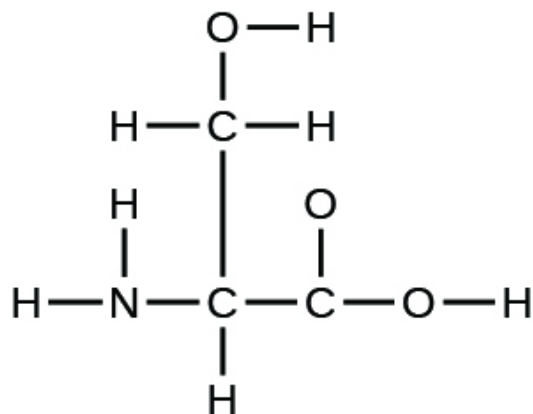


Exercise:

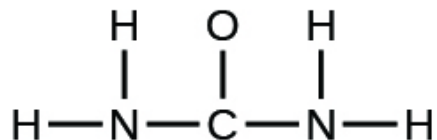
Problem:

The arrangement of atoms in several biologically important molecules is given here. Complete the Lewis structures of these molecules by adding multiple bonds and lone pairs. Do not add any more atoms.

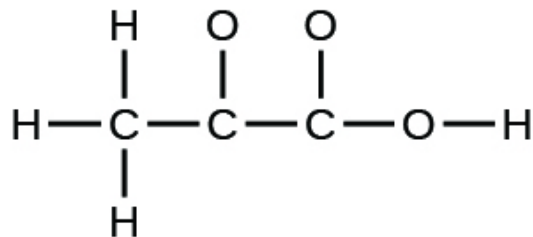
(a) the amino acid serine:



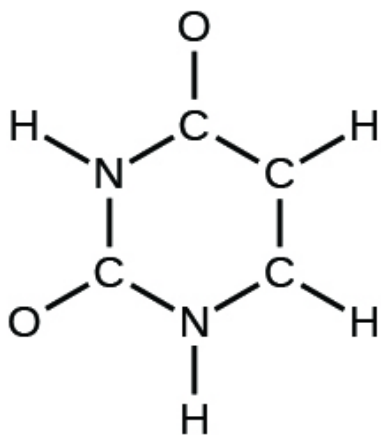
(b) urea:



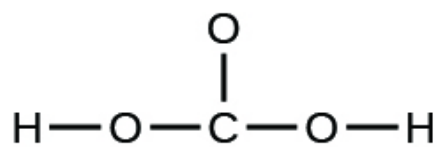
(c) pyruvic acid:



(d) uracil:

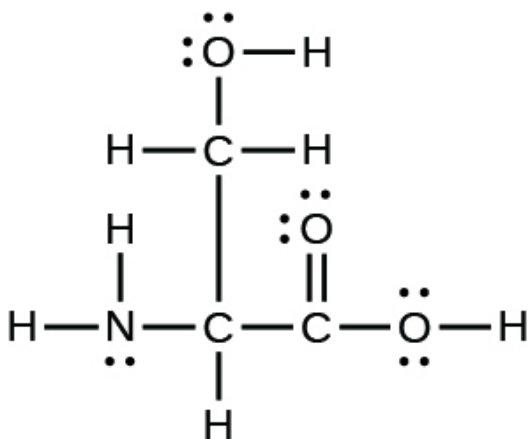


(e) carbonic acid:



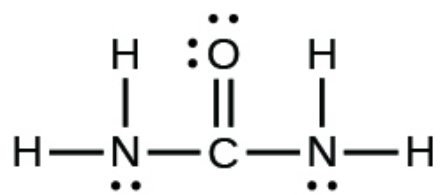
Solution:

(a)

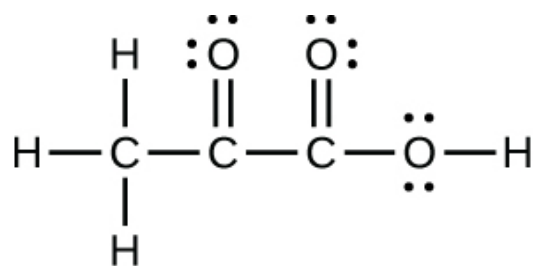


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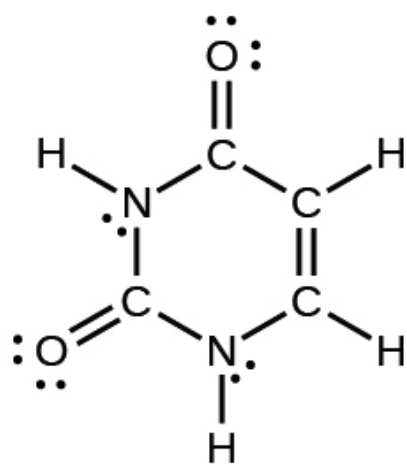
(b)



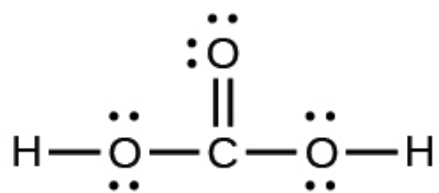
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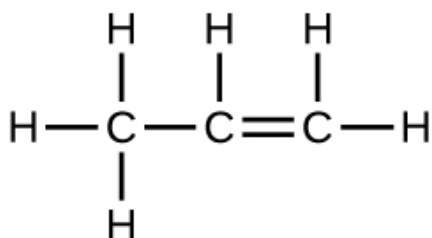
Exercise:

Problem:

A compound with a molar mass of about 28 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

Exercise:**Problem:**

A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

Solution:**Exercise:****Problem:**

Two arrangements of atoms are possible for a compound with a molar mass of about 45 g/mol that contains 52.2% C, 13.1% H, and 34.7% O by mass. Write the Lewis structures for the two molecules.

Exercise:

Problem: How are single, double, and triple bonds similar? How do they differ?

Solution:

Each bond includes a sharing of electrons between atoms. Two electrons are shared in a single bond; four electrons are shared in a double bond; and six electrons are shared in a triple bond.

Glossary

double bond

covalent bond in which two pairs of electrons are shared between two atoms

free radical

molecule that contains an odd number of electrons

hypervalent molecule

molecule containing at least one main group element that has more than eight electrons in its valence shell

Lewis structure

diagram showing lone pairs and bonding pairs of electrons in a molecule or an ion

Lewis symbol

symbol for an element or monatomic ion that uses a dot to represent each valence electron in the element or ion

lone pair

two (a pair of) valence electrons that are not used to form a covalent bond

octet rule

guideline that states main group atoms will form structures in which eight valence electrons interact with each nucleus, counting bonding electrons as interacting with both atoms connected by the bond

single bond

bond in which a single pair of electrons is shared between two atoms

triple bond

bond in which three pairs of electrons are shared between two atoms

Formal Charges and Resonance

By the end of this section, you will be able to:

- Compute formal charges for atoms in any Lewis structure
- Use formal charges to identify the most reasonable Lewis structure for a given molecule
- Explain the concept of resonance and draw Lewis structures representing resonance forms for a given molecule

In the previous section, we discussed how to write Lewis structures for molecules and polyatomic ions. As we have seen, however, in some cases, there is seemingly more than one valid structure for a molecule. We can use the concept of formal charges to help us predict the most appropriate Lewis structure when more than one is reasonable.

Calculating Formal Charge

The **formal charge** of an atom in a molecule is the *hypothetical* charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms. Another way of saying this is that formal charge results when we take the number of valence electrons of a neutral atom, subtract the nonbonding electrons, and then subtract the number of bonds connected to that atom in the Lewis structure.

Thus, we calculate formal charge as follows:

Equation:

$$\text{formal charge} = \# \text{ valence shell electrons (free atom)} - \# \text{ lone pair electrons} - \frac{1}{2} \# \text{ bonding electrons}$$

We can double-check formal charge calculations by determining the sum of the formal charges for the whole structure. The sum of the formal charges of all atoms in a molecule must be zero; the sum of the formal charges in an ion should equal the charge of the ion.

We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

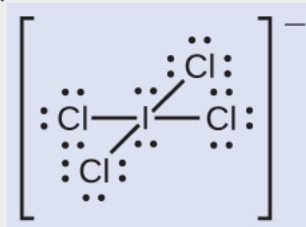
Example:

Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen ion ICl_4^- .

Solution

We divide the bonding electron pairs equally for all I–Cl bonds:



We assign lone pairs of electrons to their atoms

Subtract this number from the number of valence electrons for the neutral atom:

. Each Cl atom now has seven electrons assigned to it, and the I atom has eight.

I: $7 - 8 = -1$ Cl: $7 - 7 = 0$ The sum of the formal charges of all the atoms equals -1 , which is identical to the charge of the ion (-1) .

Check Your Learning

Calculate the formal charge for each atom in the carbon monoxide molecule:



Note:

Answer:

C -1, O +1

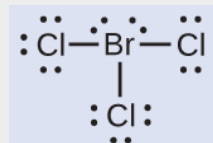
Example:

Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen molecule BrCl_3 .

Solution

Assign one of the electrons in each $\text{Br}-\text{Cl}$ bond to the Br atom and one to the Cl atom in that bond:



Assign the lone pairs to their atom. Now each Cl atom has seven electrons and the Br atom has seven electrons. Subtract this number from the number of valence electrons for the neutral atom. This gives Br: $7 - 7 = 0$ Cl: $7 - 7 = 0$ All 3 atoms have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

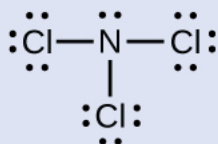
Check Your Learning

Determine the formal charge for each atom in NCl_3 .

Note:

Answer:

N: 0; all three Cl atoms: 0



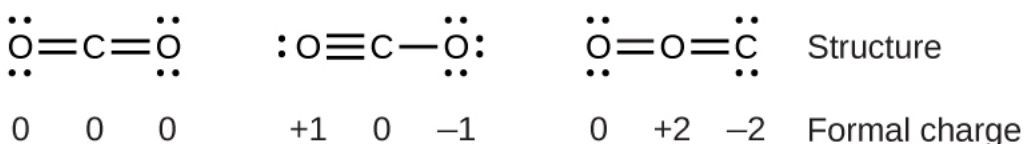
Using Formal Charge to Predict Molecular Structure

The arrangement of atoms in a molecule or ion is called its **molecular structure**. In many cases, following the steps for writing Lewis structures may lead to more than one possible molecular structure—different multiple bond and lone-pair electron placements or different arrangements of atoms, for instance. A few guidelines involving

formal charge can be helpful in deciding which of the possible structures is most likely for a particular molecule or ion:

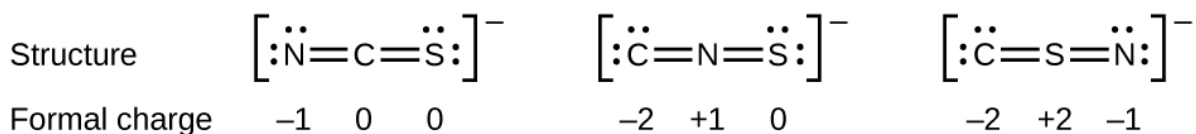
1. A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
2. If the Lewis structure must have nonzero formal charges, the arrangement with the smallest nonzero formal charges is preferable.
3. Lewis structures are preferable when adjacent formal charges are zero or of the opposite sign.
4. When we must choose among several Lewis structures with similar distributions of formal charges, the structure with the negative formal charges on the more electronegative atoms is preferable.

To see how these guidelines apply, let us consider some possible structures for carbon dioxide, CO_2 . We know from our previous discussion that the less electronegative atom typically occupies the central position, but formal charges allow us to understand *why* this occurs. We can draw three possibilities for the structure: carbon in the center and double bonds, carbon in the center with a single and triple bond, and oxygen in the center with double bonds:



Comparing the three formal charges, we can definitively identify the structure on the left as preferable because it has only formal charges of zero (Guideline 1).

As another example, the thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, could have three different molecular structures: CNS^- , NCS^- , or CSN^- . The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms. Possible Lewis structures and the formal charges for each of the three possible structures for the thiocyanate ion are shown here:

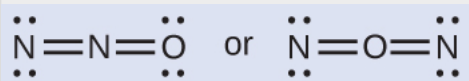


Note that the sum of the formal charges in each case is equal to the charge of the ion (-1). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges (Guideline 2). Also, it places the least electronegative atom in the center, and the negative charge on the more electronegative element (Guideline 4).

Example:

Using Formal Charge to Determine Molecular Structure

Nitrous oxide, N_2O , commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the likely structure for nitrous oxide?

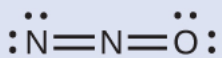


Solution

Determining formal charge yields the following:



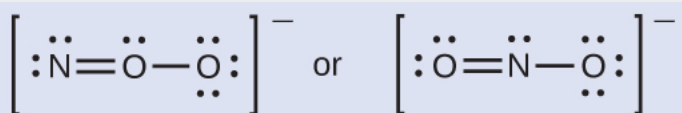
The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:



The number of atoms with formal charges are minimized (Guideline 2), and there is no formal charge larger than one (Guideline 2). This is again consistent with the preference for having the less electronegative atom in the central position.

Check Your Learning

Which is the most likely molecular structure for the nitrite (NO_2^-) ion?



Note:

Answer:



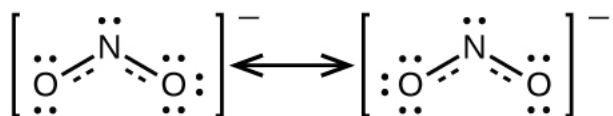
Resonance

You may have noticed that the nitrite anion in [\[link\]](#) can have two possible structures with the atoms in the same positions. The electrons involved in the N–O double bond, however, are in different positions:



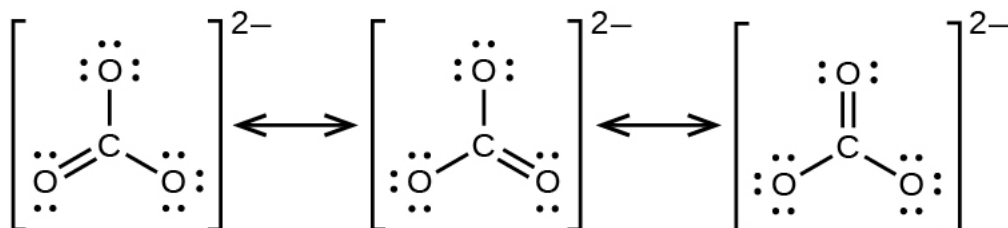
If nitrite ions do indeed contain a single and a double bond, we would expect for the two bond lengths to be different. A double bond between two atoms is shorter (and stronger) than a single bond between the same two atoms. Experiments show, however, that both N–O bonds in NO_2^- have the same strength and length, and are identical in all other properties.

It is not possible to write a single Lewis structure for NO_2^- in which nitrogen has an octet and both bonds are equivalent. Instead, we use the concept of **resonance**: if two or more Lewis structures with the same arrangement of atoms can be written for a molecule or ion, the actual distribution of electrons is an *average* of that shown by the various Lewis structures. The actual distribution of electrons in each of the nitrogen-oxygen bonds in NO_2^- is the average of a double bond and a single bond. We call the individual Lewis structures **resonance forms**. The actual electronic structure of the molecule (the average of the resonance forms) is called a **resonance hybrid** of the individual resonance forms. A double-headed arrow between Lewis structures indicates that they are resonance forms. Thus, the electronic structure of the NO_2^- ion is shown as:



We should remember that a molecule described as a resonance hybrid *never* possesses an electronic structure described by either resonance form. It does not fluctuate between resonance forms; rather, the actual electronic structure is *always* the average of that shown by all resonance forms. George Wheland, one of the pioneers of resonance theory, used a historical analogy to describe the relationship between resonance forms and resonance hybrids. A medieval traveler, having never before seen a rhinoceros, described it as a hybrid of a dragon and a unicorn because it had many properties in common with both. Just as a rhinoceros is neither a dragon sometimes nor a unicorn at other times, a resonance hybrid is neither of its resonance forms at any given time. Like a rhinoceros, it is a real entity that experimental evidence has shown to exist. It has some characteristics in common with its resonance forms, but the resonance forms themselves are convenient, imaginary images (like the unicorn and the dragon).

The carbonate anion, CO_3^{2-} , provides a second example of resonance:



One oxygen atom must have a double bond to carbon to complete the octet on the central atom. All oxygen atoms, however, are equivalent, and the double bond could form from any one of the three atoms. This gives rise to three resonance forms of the carbonate ion. Because we can write three identical resonance structures, we know that the actual arrangement of electrons in the carbonate ion is the average of the three structures. Again, experiments show that all three C–O bonds are exactly the same.

Note:



The online [Lewis Structure Make](#) includes many examples to practice drawing resonance structures.

Key Concepts and Summary

In a Lewis structure, formal charges can be assigned to each atom by treating each bond as if one-half of the electrons are assigned to each atom. These hypothetical formal charges are a guide to determining the most appropriate Lewis structure. A structure in which the formal charges are as close to zero as possible is preferred. Resonance occurs in cases where two or more Lewis structures with identical arrangements of atoms but different distributions of electrons can be written. The actual distribution of electrons (the resonance hybrid) is an average of the distribution indicated by the individual Lewis structures (the resonance forms).

Key Equations

- formal charge = # valence shell electrons (free atom) - # one pair electrons - $\frac{1}{2}$ # bonding elect

Chemistry End of Chapter Exercises

Exercise:

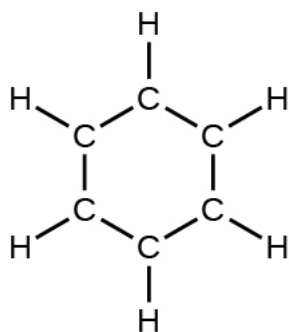
Problem: Write resonance forms that describe the distribution of electrons in each of these molecules or ions.

(a) selenium dioxide, OSeO

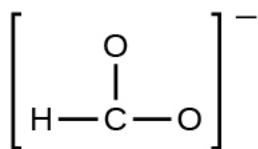
(b) nitrate ion, NO_3^-

(c) nitric acid, HNO_3 (N is bonded to an OH group and two O atoms)

(d) benzene, C_6H_6 :



(e) the formate ion:



Exercise:

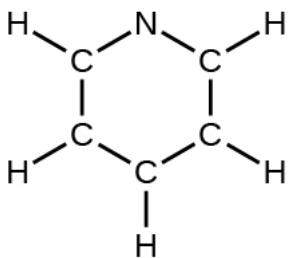
Problem: Write resonance forms that describe the distribution of electrons in each of these molecules or ions.

(a) sulfur dioxide, SO_2

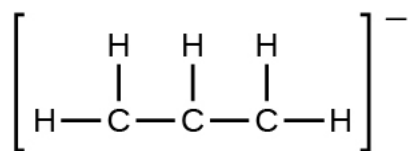
(b) carbonate ion, CO_3^{2-}

(c) hydrogen carbonate ion, HCO_3^- (C is bonded to an OH group and two O atoms)

(d) pyridine:

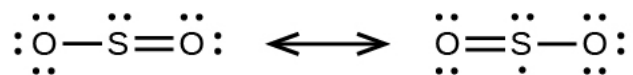


(e) the allyl ion:



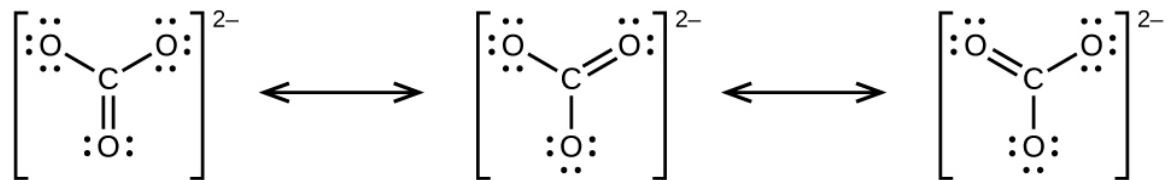
Solution:

(a)



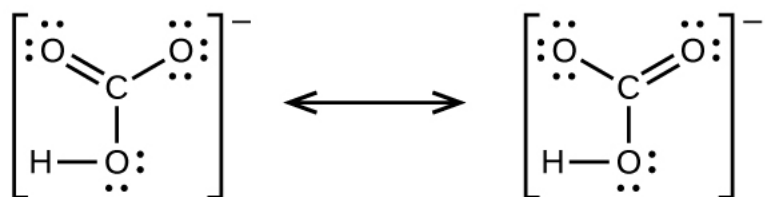
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(b)



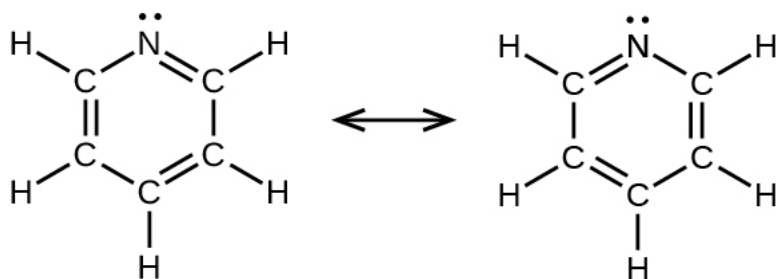
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(c)

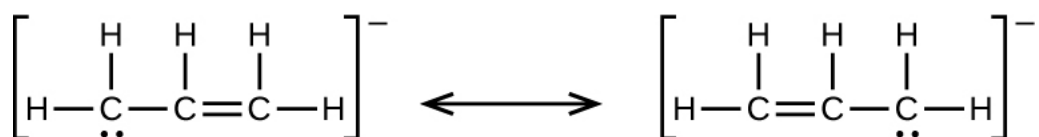


;

(d)



; (e)



Exercise:

Problem:

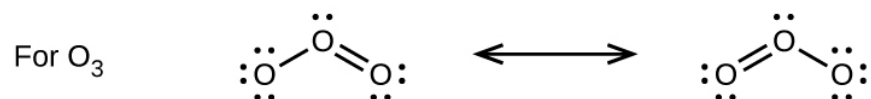
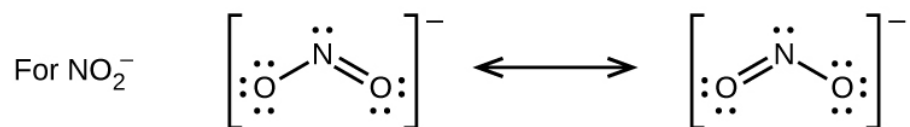
Write the resonance forms of ozone, O_3 , the component of the upper atmosphere that protects the Earth from ultraviolet radiation.

Exercise:

Problem:

Sodium nitrite, which has been used to preserve bacon and other meats, is an ionic compound. Write the resonance forms of the nitrite ion, NO_2^- .

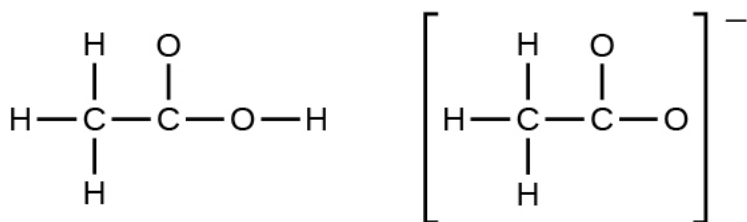
Solution:



Exercise:

Problem:

In terms of the bonds present, explain why acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, contains two distinct types of carbon-oxygen bonds, whereas the acetate ion, formed by loss of a hydrogen ion from acetic acid, only contains one type of carbon-oxygen bond. The skeleton structures of these species are shown:



Exercise:

Problem:

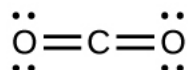
Write the Lewis structures for the following, and include resonance structures where appropriate. Indicate which has the strongest carbon-oxygen bond.

(a) CO_2

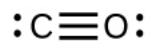
(b) CO

Solution:

(a)



(b)



CO has the strongest carbon-oxygen bond because there is a triple bond joining C and O. CO_2 has double bonds.

Exercise:

Problem:

Toothpastes containing sodium hydrogen carbonate (sodium bicarbonate) and hydrogen peroxide are widely used. Write Lewis structures for the hydrogen carbonate ion and hydrogen peroxide molecule, with resonance forms where appropriate.

Exercise:

Problem: Determine the formal charge of each element in the following:

(a) HCl

(b) CF_4

(c) PCl_3

(d) PF_5

Solution:

(a) H: 0, Cl: 0; (b) C: 0, F: 0; (c) P: 0, Cl: 0; (d) P: 0, F: 0

Exercise:

Problem: Determine the formal charge of each element in the following:

- (a) H_3O^+
- (b) SO_4^{2-}
- (c) NH_3
- (d) O_2^{2-}
- (e) H_2O_2

Exercise:

Problem: Calculate the formal charge of chlorine in the molecules Cl_2 , BeCl_2 , and ClF_5 .

Solution:

Cl in Cl_2 : 0; Cl in BeCl_2 : 0; Cl in ClF_5 : 0

Exercise:

Problem: Calculate the formal charge of each element in the following compounds and ions:

- (a) F_2CO
- (b) NO^-
- (c) BF_4^-
- (d) SnCl_3^-
- (e) H_2CCH_2
- (f) ClF_3
- (g) SeF_6
- (h) PO_4^{3-}

Exercise:

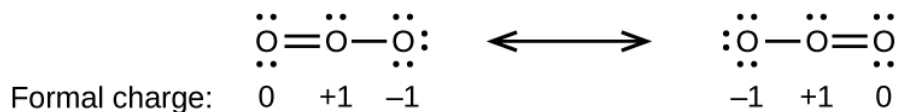
Problem:

Draw all possible resonance structures for each of these compounds. Determine the formal charge on each atom in each of the resonance structures:

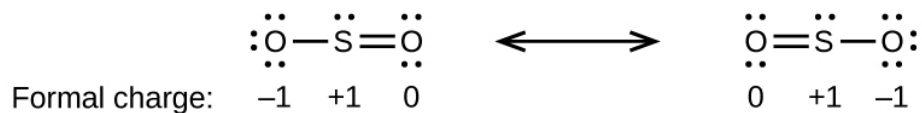
- (a) O_3
- (b) SO_2
- (c) NO_2^-
- (d) NO_3^-

Solution:

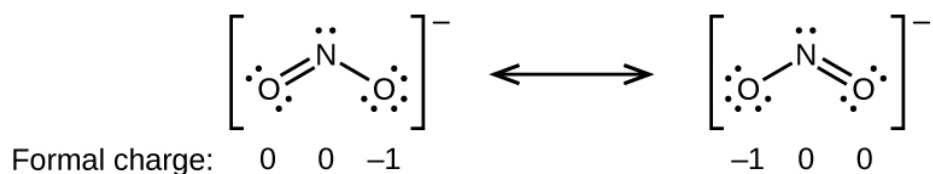
- (a)



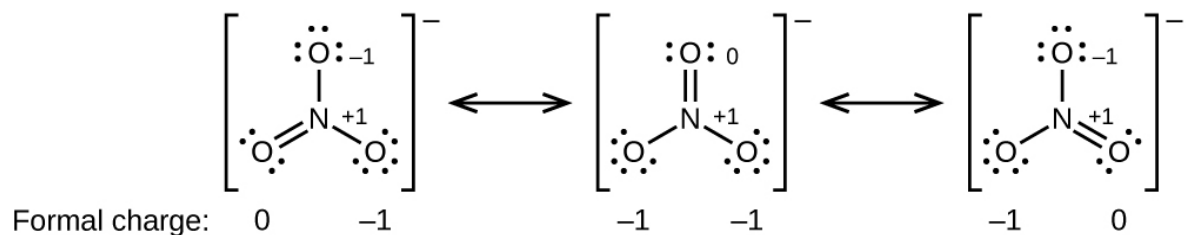
;
(b)



;
(c)



;
(d)



Exercise:

Problem:

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in nitrosyl chloride: ClNO or ClON?

Exercise:

Problem:

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in hypochlorous acid: HOCl or OClH?

Solution:

HOCl

Exercise:

Problem:

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in sulfur dioxide: OSO or SOO?

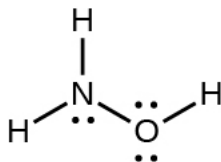
Exercise:

Problem:

Draw the structure of hydroxylamine, H_3NO , and assign formal charges; look up the structure. Is the actual structure consistent with the formal charges?

Solution:

The structure that gives zero formal charges is consistent with the actual structure:

**Exercise:****Problem:**

Iodine forms a series of fluorides (listed here). Write Lewis structures for each of the four compounds and determine the formal charge of the iodine atom in each molecule:

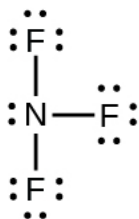
- (a) IF
- (b) IF_3
- (c) IF_5
- (d) IF_7

Exercise:**Problem:**

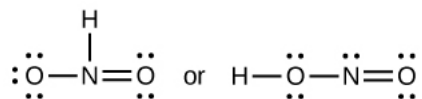
Write the Lewis structure and chemical formula of the compound with a molar mass of about 70 g/mol that contains 19.7% nitrogen and 80.3% fluorine by mass, and determine the formal charge of the atoms in this compound.

Solution:

NF_3 ;

**Exercise:**

Problem: Which of the following structures would we expect for nitrous acid? Determine the formal charges:

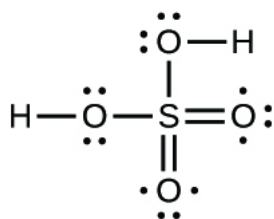


Exercise:

Problem:

Sulfuric acid is the industrial chemical produced in greatest quantity worldwide. About 90 billion pounds are produced each year in the United States alone. Write the Lewis structure for sulfuric acid, H_2SO_4 , which has two oxygen atoms and two OH groups bonded to the sulfur.

Solution:



Glossary

formal charge

charge that would result on an atom by taking the number of valence electrons on the neutral atom and subtracting the nonbonding electrons and the number of bonds (one-half of the bonding electrons)

molecular structure

arrangement of atoms in a molecule or ion

resonance

situation in which one Lewis structure is insufficient to describe the bonding in a molecule and the average of multiple structures is observed

resonance forms

two or more Lewis structures that have the same arrangement of atoms but different arrangements of electrons

resonance hybrid

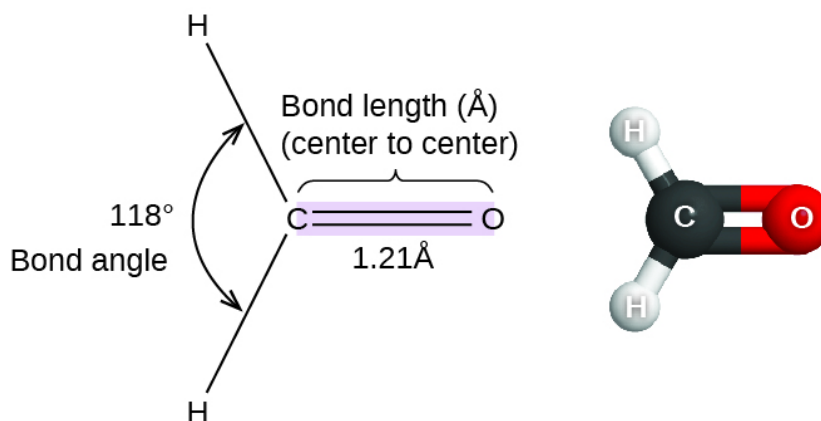
average of the resonance forms shown by the individual Lewis structures

Molecular Structure and Polarity

By the end of this section, you will be able to:

- Predict the structures of small molecules using valence shell electron pair repulsion (VSEPR) theory
- Explain the concepts of polar covalent bonds and molecular polarity
- Assess the polarity of a molecule based on its bonding and structure

Thus far, we have used two-dimensional Lewis structures to represent molecules. However, molecular structure is actually three-dimensional, and it is important to be able to describe molecular bonds in terms of their distances, angles, and relative arrangements in space ([\[link\]](#)). A **bond angle** is the angle between any two bonds that include a common atom, usually measured in degrees. A **bond distance** (or bond length) is the distance between the nuclei of two bonded atoms along the straight line joining the nuclei. Bond distances are measured in Ångstroms ($1 \text{ Å} = 10^{-10} \text{ m}$) or picometers ($1 \text{ pm} = 10^{-12} \text{ m}$, $100 \text{ pm} = 1 \text{ Å}$).



Bond distances (lengths) and angles are shown for the formaldehyde molecule, H₂CO.

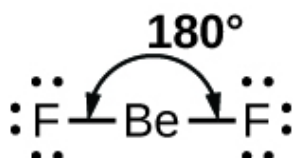
VSEPR Theory

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that

electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

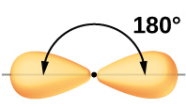
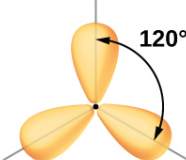
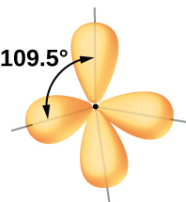
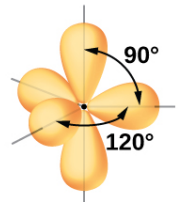
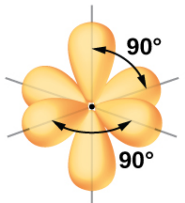
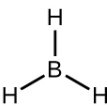
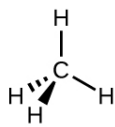


As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 ([\[link\]](#)) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° ([\[link\]](#)).



The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

[\[link\]](#) illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a

linear geometry; three regions form a **trigonal planar** geometry; four regions form a **tetrahedral** geometry; five regions form a **trigonal bipyramidal** geometry; and six regions form an **octahedral** geometry.

Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation	$\text{H}-\text{Be}-\text{H}$				
Electron pair geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

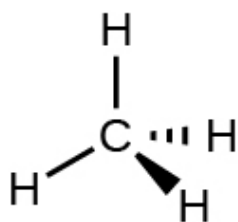
The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

Electron-pair Geometry versus Molecular Structure

It is important to note that electron-pair geometry around a central atom is *not* the same thing as its molecular structure. The electron-pair geometries shown in [\[link\]](#) describe all regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms*, not the electrons.

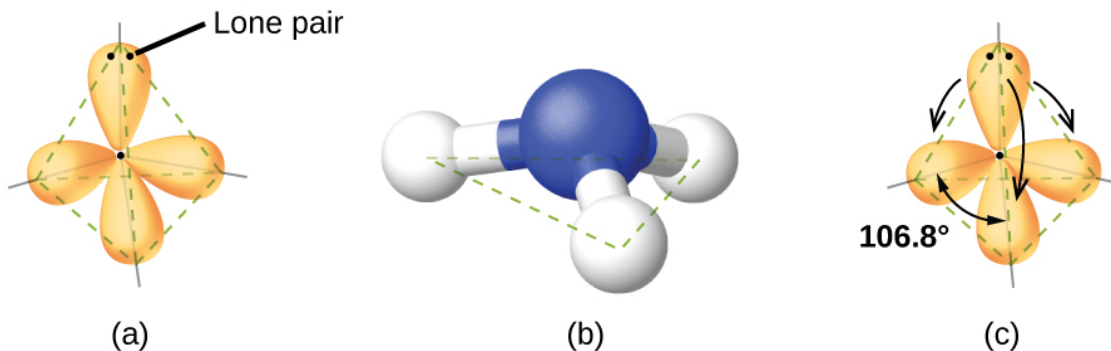
We differentiate between these two situations by naming the geometry that includes *all* electron pairs the **electron-pair geometry**. The structure that includes only the placement of the atoms in the molecule is called the **molecular structure**. The electron-pair geometries will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.

For example, the methane molecule, CH_4 , which is the major component of natural gas, has four bonding pairs of electrons around the central carbon atom; the electron-pair geometry is tetrahedral, as is the molecular structure ([\[link\]](#)). On the other hand, the ammonia molecule, NH_3 , also has four electron pairs associated with the nitrogen atom, and thus has a tetrahedral electron-pair geometry. One of these regions, however, is a lone pair, which is not included in the molecular structure, and this lone pair influences the shape of the molecule ([\[link\]](#)).



The
molecular
structure of
the methane
molecule,
 CH_4 , is
shown with

a
tetrahedral
arrangement
of the
hydrogen
atoms.
VSEPR
structures
like this one
are often
drawn using
the wedge
and dash
notation, in
which solid
lines
represent
bonds in the
plane of the
page, solid
wedges
represent
bonds
coming up
out of the
plane, and
dashed lines
represent
bonds going
down into
the plane.



(a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than 109.5° .

As seen in [\[link\]](#), small distortions from the ideal angles in [\[link\]](#) can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. The order of electron-pair repulsions from greatest to least repulsion is:

Equation:

lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

This order of repulsions determines the amount of space occupied by different regions of electrons. A lone pair of electrons occupies a larger region of space than the electrons in a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on. The order of sizes from largest to smallest is:


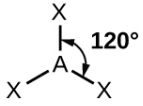
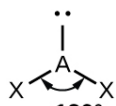
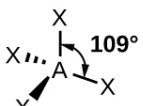


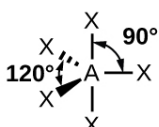
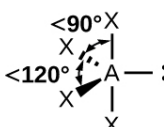
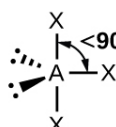
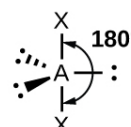
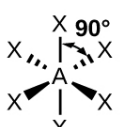
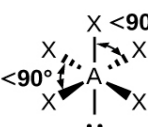
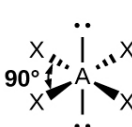


Equation:

lone pair > triple bond > double bond > single bond

Consider formaldehyde, H_2CO , which is used as a preservative for biological and anatomical specimens ([\[link\]](#)). This molecule has regions of high electron

density that consist of two single bonds and one double bond. The basic geometry is trigonal planar with 120° bond angles, but we see that the double bond causes slightly larger angles (121°), and the angle between the single bonds is slightly smaller (118°).

In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid ([\[link\]](#)) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Again, there are slight deviations from the ideal because lone pairs occupy larger regions of space than do bonding electrons. The H–N–H bond angles in NH_3 are slightly smaller than the 109.5° angle in a regular tetrahedron ([\[link\]](#)) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion ([\[link\]](#)). [\[link\]](#) illustrates the ideal molecular structures, which are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.

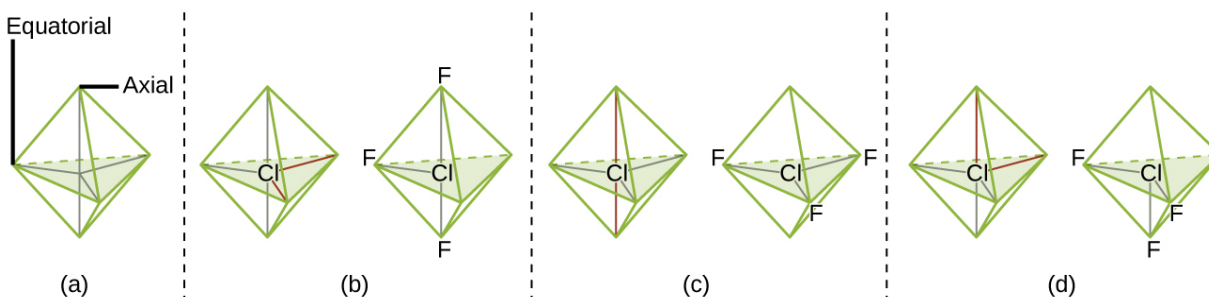
Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
5	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square pyramid	 Square planar	 T-shape	 Linear

The molecular structures are identical to the electron-pair geometries when there are no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry.

According to VSEPR theory, the terminal atom locations (Xs in [\[link\]](#)) are equivalent within the linear, trigonal planar, and tetrahedral electron-pair geometries (the first three rows of the table). It does not matter which X is replaced with a lone pair because the molecules can be rotated to convert positions. For trigonal bipyramidal electron-pair geometries, however, there are two distinct X positions, as shown in [\[link\]](#): an **axial position** (if we hold a model of a trigonal bipyramid by the two axial positions, we have an axis

around which we can rotate the model) and an **equatorial position** (three positions form an equator around the middle of the molecule). As shown in [\[link\]](#), the axial position is surrounded by bond angles of 90° , whereas the equatorial position has more space available because of the 120° bond angles. In a trigonal bipyramidal electron-pair geometry, lone pairs always occupy equatorial positions because these more spacious positions can more easily accommodate the larger lone pairs.

Theoretically, we can come up with three possible arrangements for the three bonds and two lone pairs for the ClF_3 molecule ([\[link\]](#)). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.



(a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in ClF_3 have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions.

When a central atom has two lone electron pairs and four bonding regions, we have an octahedral electron-pair geometry. The two lone pairs are on opposite sides of the octahedron (180° apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions ([\[link\]](#)).

Predicting Electron Pair Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:

1. Write the Lewis structure of the molecule or polyatomic ion.
2. Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.
3. Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral ([link](#), first column).
4. Use the number of lone pairs to determine the molecular structure ([link](#)). If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

The following examples illustrate the use of VSEPR theory to predict the molecular structure of molecules or ions that have no lone pairs of electrons. In this case, the molecular structure is identical to the electron pair geometry.

Example:

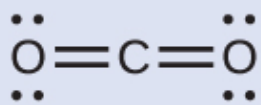
Predicting Electron-pair Geometry and Molecular Structure: CO₂ and BCl₃

Predict the electron-pair geometry and molecular structure for each of the following:

- (a) carbon dioxide, CO₂, a molecule produced by the combustion of fossil fuels
- (b) boron trichloride, BCl₃, an important industrial chemical

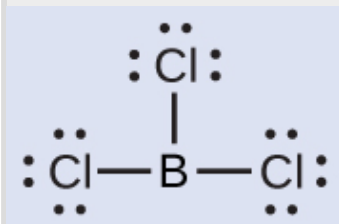
Solution

- (a) We write the Lewis structure of CO₂ as:

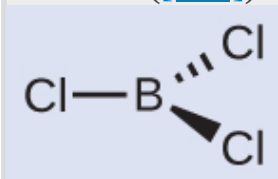


This shows us two regions of high electron density around the carbon atom—each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond angle of 180° . The electron-pair geometry and molecular structure are identical, and CO_2 molecules are linear.

(b) We write the Lewis structure of BCl_3 as:



Thus we see that BCl_3 contains three bonds, and there are no lone pairs of electrons on boron. The arrangement of three regions of high electron density gives a trigonal planar electron-pair geometry. The B–Cl bonds lie in a plane with 120° angles between them. BCl_3 also has a trigonal planar molecular structure ([link](#)).



The electron-pair geometry and molecular structure of BCl_3 are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles (120°), unlike the Lewis structure shown above.

Check Your Learning

Carbonate, CO_3^{2-} , is a common polyatomic ion found in various materials from eggshells to antacids. What are the electron-pair geometry and molecular structure of this polyatomic ion?

Note:

Answer:

The electron-pair geometry is trigonal planar and the molecular structure is trigonal planar. Due to resonance, all three C–O bonds are identical. Whether they are single, double, or an average of the two, each bond counts as one region of electron density.

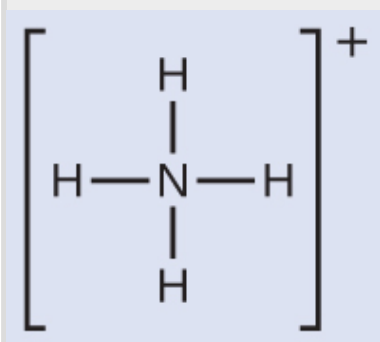
Example:**Predicting Electron-pair Geometry and Molecular Structure: Ammonium**

Two of the top 50 chemicals produced in the United States, ammonium nitrate and ammonium sulfate, both used as fertilizers, contain the ammonium ion.

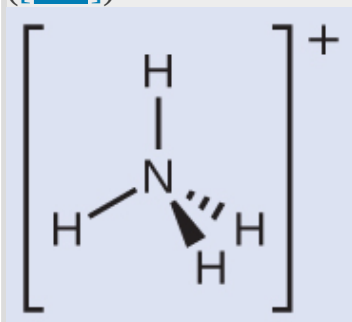
Predict the electron-pair geometry and molecular structure of the NH_4^+ cation.

Solution

We write the Lewis structure of NH_4^+ as:



We can see that NH_4^+ contains four bonds from the nitrogen atom to hydrogen atoms and no lone pairs. We expect the four regions of high electron density to arrange themselves so that they point to the corners of a tetrahedron with the central nitrogen atom in the middle ([link](#)). Therefore, the electron pair geometry of NH_4^+ is tetrahedral, and the molecular structure is also tetrahedral ([link](#)).



The ammonium ion displays a tetrahedral

electron-pair
geometry as well
as a tetrahedral
molecular
structure.

Check Your Learning

Identify a molecule with trigonal bipyramidal molecular structure.

Note:

Answer:

Any molecule with five electron pairs around the central atoms including no lone pairs will be trigonal bipyramidal. PF_5 is a common example.

The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

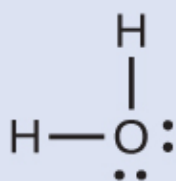
Example:

Predicting Electron-pair Geometry and Molecular Structure: Lone Pairs on the Central Atom

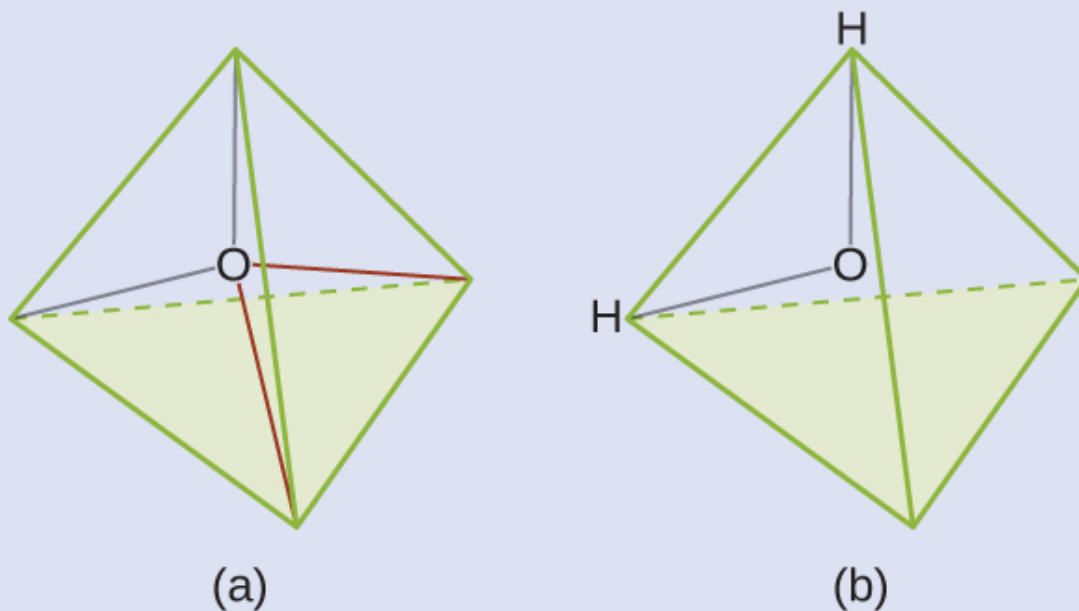
Predict the electron-pair geometry and molecular structure of a water molecule.

Solution

The Lewis structure of H_2O indicates that there are four regions of high electron density around the oxygen atom: two lone pairs and two chemical bonds:



We predict that these four regions are arranged in a tetrahedral fashion ([link](#)), as indicated in [link](#). Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than 109.5° . In fact, the bond angle is 104.5° .



(a) H_2O has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent.

Check Your Learning

The hydronium ion, H_3O^+ , forms when acids are dissolved in water. Predict the electron-pair geometry and molecular structure of this cation.

Note:

Answer:

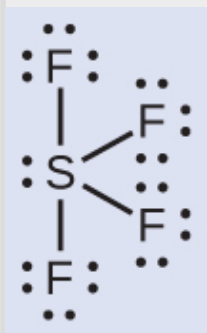
electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal

Example:**Predicting Electron-pair Geometry and Molecular Structure: SF₄**

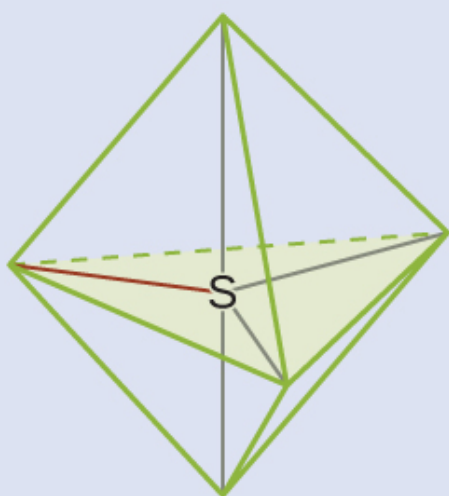
Sulfur tetrafluoride, SF₄, is extremely valuable for the preparation of fluorine-containing compounds used as herbicides (i.e., SF₄ is used as a fluorinating agent). Predict the electron-pair geometry and molecular structure of a SF₄ molecule.

Solution

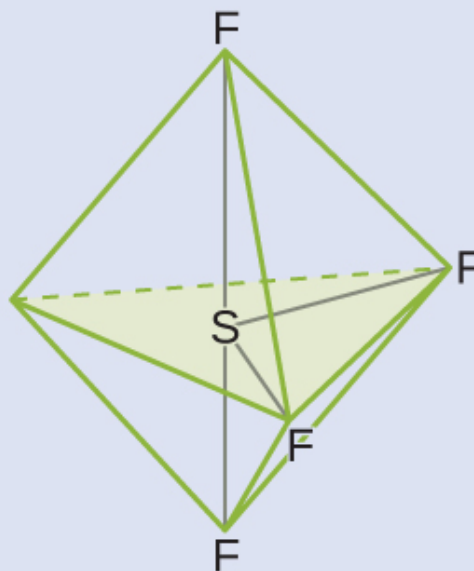
The Lewis structure of SF₄ indicates five regions of electron density around the sulfur atom: one lone pair and four bonding pairs:



We expect these five regions to adopt a trigonal bipyramidal electron-pair geometry. To minimize lone pair repulsions, the lone pair occupies one of the equatorial positions. The molecular structure ([\[link\]](#)) is that of a seesaw ([\[link\]](#)).



(a)



(b)

(a) SF₄ has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure.

Check Your Learning

Predict the electron pair geometry and molecular structure for molecules of XeF₂.

Note:

Answer:

The electron-pair geometry is trigonal bipyramidal. The molecular structure is linear.

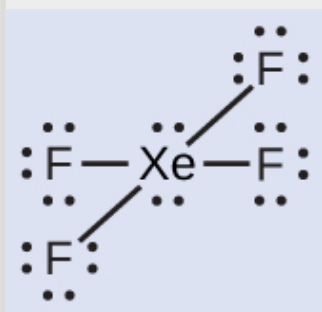
Example:

Predicting Electron-pair Geometry and Molecular Structure: XeF₄

Of all the noble gases, xenon is the most reactive, frequently reacting with elements such as oxygen and fluorine. Predict the electron-pair geometry and molecular structure of the XeF₄ molecule.

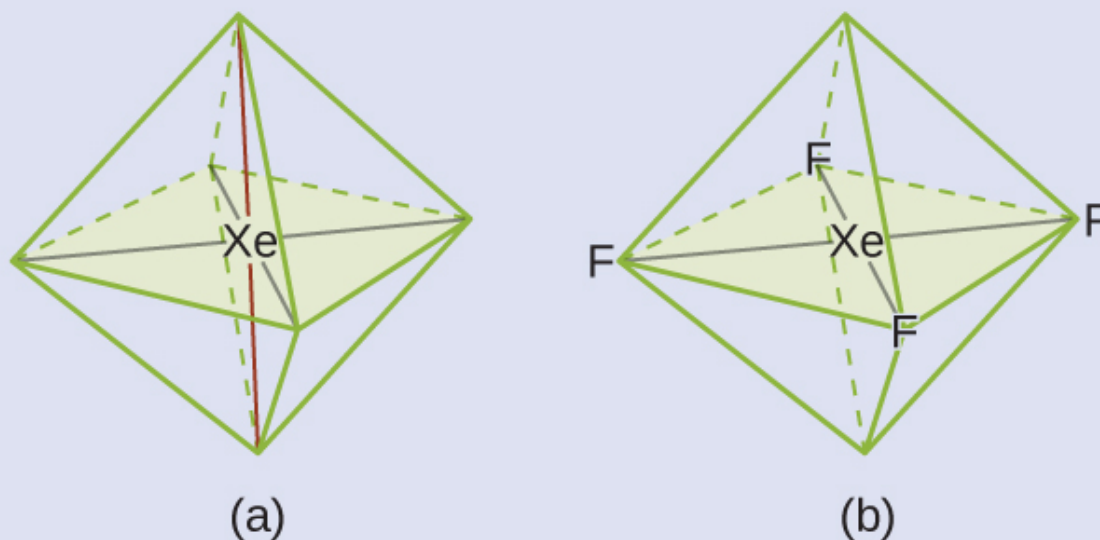
Solution

The Lewis structure of XeF₄ indicates six regions of high electron density around the xenon atom: two lone pairs and four bonds:



These six regions adopt an octahedral arrangement ([link](#)), which is the electron-pair geometry. To minimize repulsions, the lone pairs should be on

opposite sides of the central atom ([link](#)). The five atoms are all in the same plane and have a square planar molecular structure.



(a) XeF₄ adopts an octahedral arrangement with two lone pairs (red lines) and four bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another.

Check Your Learning

In a certain molecule, the central atom has three lone pairs and two bonds. What will the electron pair geometry and molecular structure be?

Note:

Answer:

electron pair geometry: trigonal bipyramidal; molecular structure: linear

Molecular Structure for Multicenter Molecules

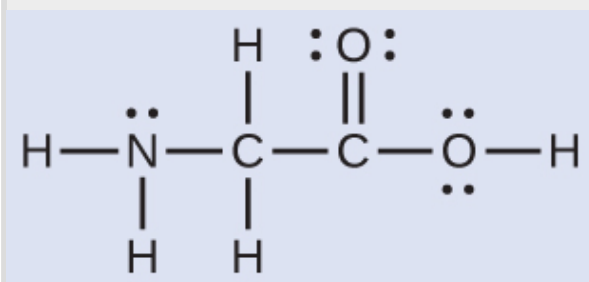
When a molecule or polyatomic ion has only one central atom, the molecular structure completely describes the shape of the molecule. Larger molecules do

not have a single central atom, but are connected by a chain of interior atoms that each possess a “local” geometry. The way these local structures are oriented with respect to each other also influences the molecular shape, but such considerations are largely beyond the scope of this introductory discussion. For our purposes, we will only focus on determining the local structures.

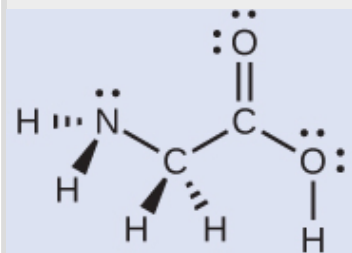
Example:

Predicting Structure in Multicenter Molecules

The Lewis structure for the simplest amino acid, glycine, $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$, is shown here. Predict the local geometry for the nitrogen atom, the two carbon atoms, and the oxygen atom with a hydrogen atom attached:



Solution



Consider each central atom independently. The electron-pair geometries:

- nitrogen—four regions of electron density; tetrahedral
- carbon (CH_2)—four regions of electron density; tetrahedral
- carbon (CO_2)—three regions of electron density; trigonal planar
- oxygen (OH)—four regions of electron density; tetrahedral

The local structures:

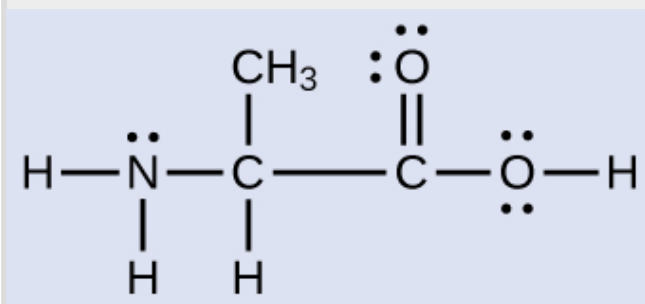
- nitrogen—three bonds, one lone pair; trigonal pyramidal

- carbon ($\underline{\text{C}}\text{H}_2$)—four bonds, no lone pairs; tetrahedral
- carbon ($\underline{\text{C}}\text{O}_2$)—three bonds (double bond counts as one bond), no lone pairs; trigonal planar
- oxygen ($\underline{\text{O}}\text{H}$)—two bonds, two lone pairs; bent (109°)

Check Your Learning

Another amino acid is alanine, which has the Lewis structure shown here.

Predict the electron-pair geometry and local structure of the nitrogen atom, the three carbon atoms, and the oxygen atom with hydrogen attached:



Note:

Answer:

electron-pair geometries: nitrogen—tetrahedral; carbon ($\underline{\text{C}}\text{H}$)—tetrahedral; carbon ($\underline{\text{C}}\text{H}_3$)—tetrahedral; carbon ($\underline{\text{C}}\text{O}_2$)—trigonal planar; oxygen ($\underline{\text{O}}\text{H}$)—tetrahedral; local structures: nitrogen—trigonal pyramidal; carbon ($\underline{\text{C}}\text{H}$)—tetrahedral; carbon ($\underline{\text{C}}\text{H}_3$)—tetrahedral; carbon ($\underline{\text{C}}\text{O}_2$)—trigonal planar; oxygen ($\underline{\text{O}}\text{H}$)—bent (109°)

Note:

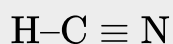


The [molecular shape simulator](#) lets you build various molecules and practice naming their electron-pair geometries and molecular structures.

Example:**Molecular Simulation**

Using [molecular shape simulator](#) allows us to control whether bond angles and/or lone pairs are displayed by checking or unchecking the boxes under “Options” on the right. We can also use the “Name” checkboxes at bottom-left to display or hide the electron pair geometry (called “electron geometry” in the simulator) and/or molecular structure (called “molecular shape” in the simulator).

Build the molecule HCN in the simulator based on the following Lewis structure:

Equation:

Click on each bond type or lone pair at right to add that group to the central atom. Once you have the complete molecule, rotate it to examine the predicted molecular structure. What molecular structure is this?

Solution

The molecular structure is linear.

Check Your Learning

Build a more complex molecule in the simulator. Identify the electron-group geometry, molecular structure, and bond angles. Then try to find a chemical formula that would match the structure you have drawn.

Note:**Answer:**

Answers will vary. For example, an atom with four single bonds, a double bond, and a lone pair has an octahedral electron-group geometry and a square pyramidal molecular structure. XeOF_4 is a molecule that adopts this structure.

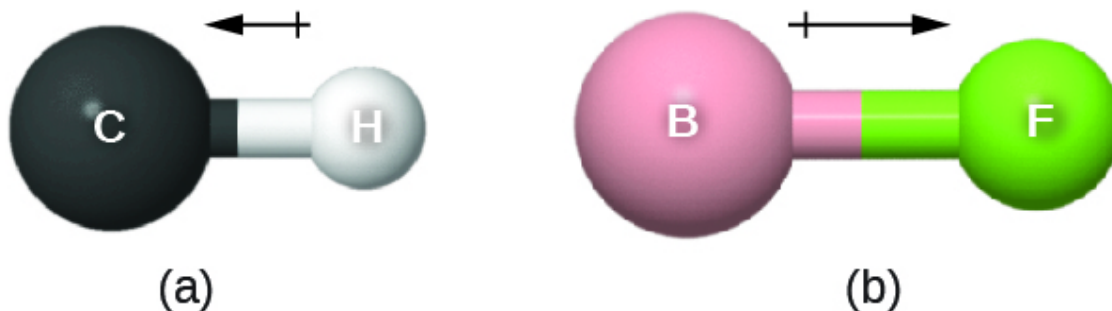
Molecular Polarity and Dipole Moment

As discussed previously, polar covalent bonds connect two atoms with differing electronegativities, leaving one atom with a partial positive charge (δ^+) and the other atom with a partial negative charge (δ^-), as the electrons are pulled toward the more electronegative atom. This separation of charge gives rise to a **bond dipole moment**. The magnitude of a bond dipole moment is represented by the Greek letter mu (μ) and is given by the formula shown here, where Q is the magnitude of the partial charges (determined by the electronegativity difference) and r is the distance between the charges:

Equation:

$$\mu = Qr$$

This bond moment can be represented as a **vector**, a quantity having both direction and magnitude ([\[link\]](#)). Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom. A small plus sign is drawn on the less electronegative end to indicate the partially positive end of the bond. The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms.



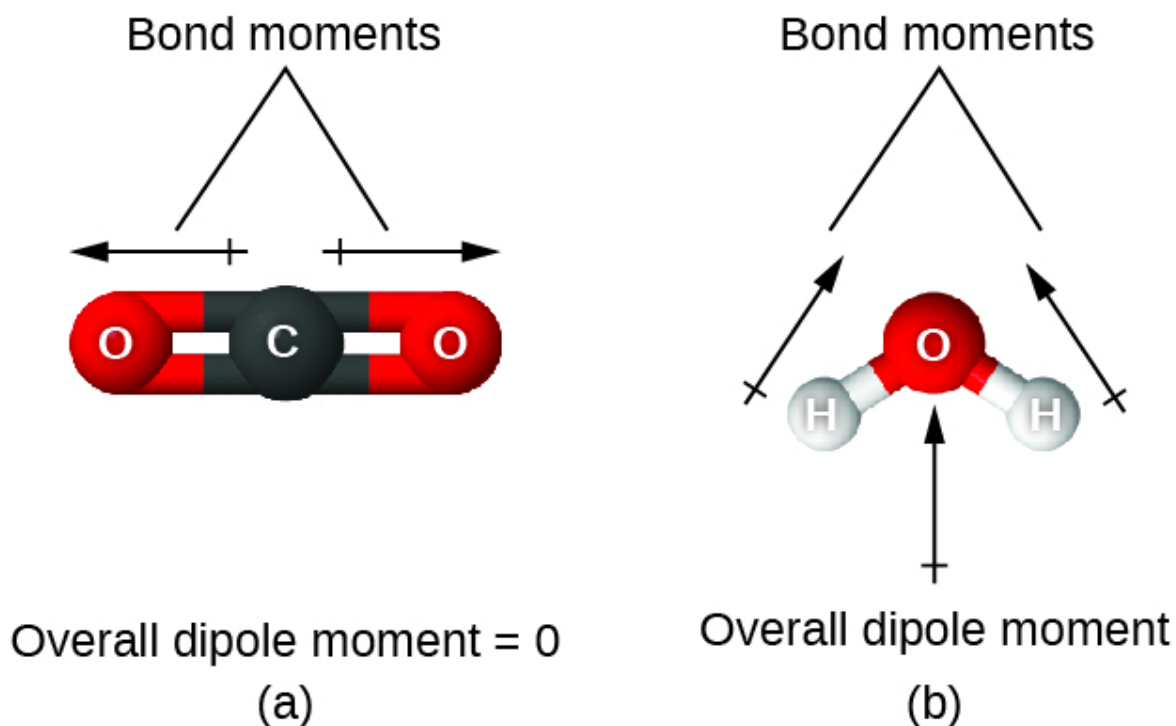
(a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.

A whole molecule may also have a separation of charge, depending on its molecular structure and the polarity of each of its bonds. If such a charge separation exists, the molecule is said to be a **polar molecule** (or dipole); otherwise the molecule is said to be nonpolar. The **dipole moment** measures the extent of net charge separation in the molecule as a whole. We determine the dipole moment by adding the bond moments in three-dimensional space, taking into account the molecular structure.

For diatomic molecules, there is only one bond, so its bond dipole moment determines the molecular polarity. Homonuclear diatomic molecules such as Br_2 and N_2 have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as CO , there is a small dipole moment. For HF , there is a larger dipole moment because there is a larger difference in electronegativity.

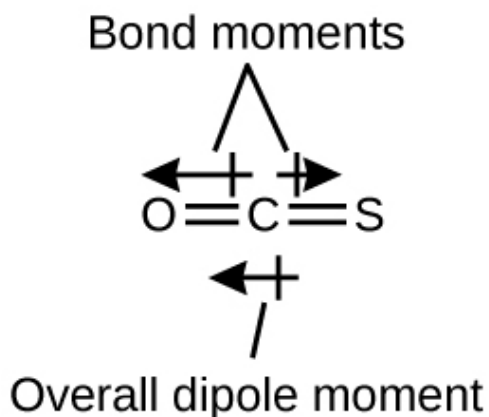
When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel (vector sum equals zero), then the molecule is nonpolar. This is the situation in CO_2 ([link](#)). Each of the bonds is polar, but the molecule as a whole is nonpolar. From the Lewis structure, and using VSEPR theory, we determine that the CO_2 molecule is linear with polar $\text{C}=\text{O}$ bonds on opposite sides of the carbon atom. The bond moments cancel because they are pointed in opposite directions. In the case of the water molecule ([link](#)), the Lewis structure again shows that there are two bonds to a central atom, and the electronegativity

difference again shows that each of these bonds has a nonzero bond moment. In this case, however, the molecular structure is bent because of the lone pairs on O, and the two bond moments do not cancel. Therefore, water does have a net dipole moment and is a polar molecule (dipole).



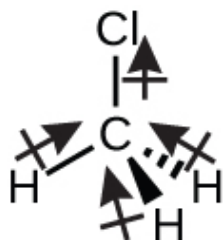
The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out.

The OCS molecule has a structure similar to CO_2 , but a sulfur atom has replaced one of the oxygen atoms. To determine if this molecule is polar, we draw the molecular structure. VSEPR theory predicts a linear molecule:

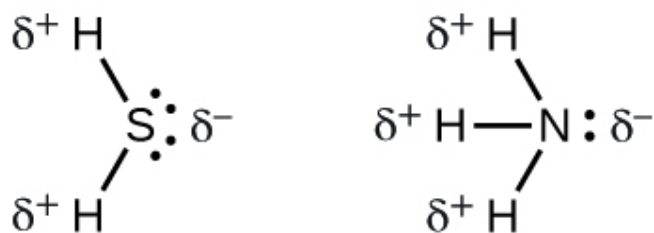


The C-O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C-S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

Chloromethane, CH_3Cl , is another example of a polar molecule. Although the polar C-Cl and C-H bonds are arranged in a tetrahedral geometry, the C-Cl bonds have a larger bond moment than the C-H bond, and the bond moments do not completely cancel each other. All of the dipoles have an upward component in the orientation shown, since carbon is more electronegative than hydrogen and less electronegative than chlorine:



When we examine the highly symmetrical molecules BF_3 (trigonal planar), CH_4 (tetrahedral), PF_5 (trigonal bipyramidal), and SF_6 (octahedral), in which all the polar bonds are identical, the molecules are nonpolar. The bonds in these molecules are arranged such that their dipoles cancel. However, just because a molecule contains identical bonds does not mean that the dipoles will always cancel. Many molecules that have identical bonds and lone pairs on the central atoms have bond dipoles that do not cancel. Examples include H_2S and NH_3 . A hydrogen atom is at the positive end and a nitrogen or sulfur atom is at the negative end of the polar bonds in these molecules:

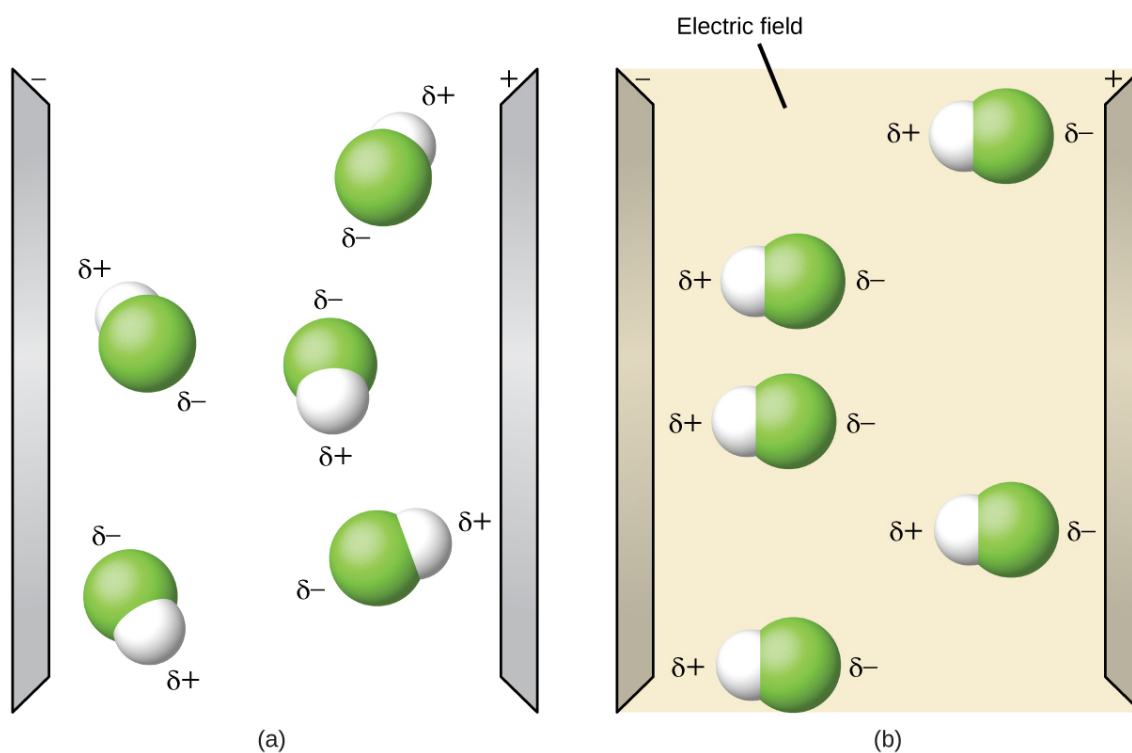


To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment does not cancel.

Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate ([link](#)). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.



(a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

Note:



The [molecule polarity simulation](#) provides many ways to explore dipole moments of bonds and molecules.

Example:**Polarity Simulations**

Open the [molecule polarity simulation](#) and select the “Three Atoms” tab at the top. This should display a molecule ABC with three electronegativity adjusters. You can display or hide the bond moments, molecular dipoles, and partial charges at the right. Turning on the Electric Field will show whether the molecule moves when exposed to a field, similar to [\[link\]](#).

Use the electronegativity controls to determine how the molecular dipole will look for the starting bent molecule if:

- (a) A and C are very electronegative and B is in the middle of the range.
- (b) A is very electronegative, and B and C are not.

Solution

- (a) Molecular dipole moment points immediately between A and C.
- (b) Molecular dipole moment points along the A–B bond, toward A.

Check Your Learning

Determine the partial charges that will give the largest possible bond dipoles.

Note:**Answer:**

The largest bond moments will occur with the largest partial charges. The two solutions above represent how unevenly the electrons are shared in the bond. The bond moments will be maximized when the electronegativity difference is greatest. The controls for A and C should be set to one extreme, and B should be set to the opposite extreme. Although the magnitude of the bond moment will not change based on whether B is the most electronegative or the least, the direction of the bond moment will.

Key Concepts and Summary

VSEPR theory predicts the three-dimensional arrangement of atoms in a molecule. It states that valence electrons will assume an electron-pair geometry that minimizes repulsions between areas of high electron density (bonds and/or lone pairs). Molecular structure, which refers only to the placement of atoms in

a molecule and not the electrons, is equivalent to electron-pair geometry only when there are no lone electron pairs around the central atom. A dipole moment measures a separation of charge. For one bond, the bond dipole moment is determined by the difference in electronegativity between the two atoms. For a molecule, the overall dipole moment is determined by both the individual bond moments and how these dipoles are arranged in the molecular structure. Polar molecules (those with an appreciable dipole moment) interact with electric fields, whereas nonpolar molecules do not.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Explain why the HOH molecule is bent, whereas the HBeH molecule is linear.

Solution:

The placement of the two sets of unpaired electrons in water forces the bonds to assume a tetrahedral arrangement, and the resulting HOH molecule is bent. The HBeH molecule (in which Be has only two electrons to bond with the two electrons from the hydrogens) must have the electron pairs as far from one another as possible and is therefore linear.

Exercise:

Problem:

What feature of a Lewis structure can be used to tell if a molecule's (or ion's) electron-pair geometry and molecular structure will be identical?

Exercise:

Problem:

Explain the difference between electron-pair geometry and molecular structure.

Solution:

Space must be provided for each pair of electrons whether they are in a bond or are present as lone pairs. Electron-pair geometry considers the placement of all electrons. Molecular structure considers only the bonding-pair geometry.

Exercise:

Problem:

Why is the H–N–H angle in NH_3 smaller than the H–C–H bond angle in CH_4 ? Why is the H–N–H angle in NH_4^+ identical to the H–C–H bond angle in CH_4 ?

Exercise:

Problem:

Explain how a molecule that contains polar bonds can be nonpolar.

Solution:

As long as the polar bonds are compensated (for example, two identical atoms are found directly across the central atom from one another), the molecule can be nonpolar.

Exercise:

Problem:

As a general rule, MX_n molecules (where M represents a central atom and X represents terminal atoms; $n = 2 - 5$) are polar if there is one or more lone pairs of electrons on M. NH_3 (M = N, X = H, $n = 3$) is an example. There are two molecular structures with lone pairs that are exceptions to this rule. What are they?

Exercise:

Problem:

Predict the electron pair geometry and the molecular structure of each of the following molecules or ions:

(a) SF_6

(b) PCl_5



Solution:

(a) Both the electron geometry and the molecular structure are octahedral.

(b) Both the electron geometry and the molecular structure are trigonal bipyramid.

(c) Both the electron geometry and the molecular structure are linear.

(d) Both the electron geometry and the molecular structure are trigonal planar.

Exercise:

Problem:

Identify the electron pair geometry and the molecular structure of each of the following molecules or ions:



Exercise:

Problem:

What are the electron-pair geometry and the molecular structure of each of the following molecules or ions?



(d) PCl_3

(e) SeF_4

(f) PH_2^-

Solution:

(a) electron-pair geometry: octahedral, molecular structure: square pyramidal; (b) electron-pair geometry: tetrahedral, molecular structure: bent; (c) electron-pair geometry: octahedral, molecular structure: square planar; (d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; (e) electron-pair geometry: trigonal bipyramidal, molecular structure: seesaw; (f) electron-pair geometry: tetrahedral, molecular structure: bent (109°)

Exercise:

Problem:

Predict the electron pair geometry and the molecular structure of each of the following ions:

(a) H_3O^+

(b) PCl_4^-

(c) SnCl_3^-

(d) BrCl_4^-

(e) ICl_3

(f) XeF_4

(g) SF_2

Exercise:

Problem:

Identify the electron pair geometry and the molecular structure of each of the following molecules:

- (a) ClNO (N is the central atom)
 - (b) CS_2
 - (c) Cl_2CO (C is the central atom)
 - (d) Cl_2SO (S is the central atom)
 - (e) SO_2F_2 (S is the central atom)
 - (f) XeO_2F_2 (Xe is the central atom)
 - (g) ClOF_2^+ (Cl is the central atom)
-

Solution:

(a) electron-pair geometry: trigonal planar, molecular structure: bent (120°); (b) electron-pair geometry: linear, molecular structure: linear; (c) electron-pair geometry: trigonal planar, molecular structure: trigonal planar; (d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; (e) electron-pair geometry: tetrahedral, molecular structure: tetrahedral; (f) electron-pair geometry: trigonal bipyramidal, molecular structure: seesaw; (g) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal

Exercise:

Problem:

Predict the electron pair geometry and the molecular structure of each of the following:

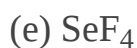
- (a) IOF_5 (I is the central atom)
- (b) POCl_3 (P is the central atom)
- (c) Cl_2SeO (Se is the central atom)
- (d) ClSO^+ (S is the central atom)
- (e) F_2SO (S is the central atom)



Exercise:

Problem:

Which of the following molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?



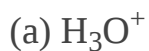
Solution:

All of these molecules and ions contain polar bonds. Only ClF_5 , ClO_2^- , PCl_3 , SeF_4 , and PH_2^- have dipole moments.

Exercise:

Problem:

Which of these molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?





Exercise:

Problem: Which of the following molecules have dipole moments?

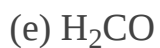
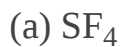


Solution:

SeS_2 , CCl_2F_2 , PCl_3 , and ClNO all have dipole moments.

Exercise:

Problem: Identify the molecules with a dipole moment:



Exercise:

Problem:

The molecule XF_3 has a dipole moment. Is X boron or phosphorus?

Solution:

P

Exercise:**Problem:**

The molecule XCl_2 has a dipole moment. Is X beryllium or sulfur?

Exercise:

Problem: Is the Cl_2BBCl_2 molecule polar or nonpolar?

Solution:

nonpolar

Exercise:**Problem:**

There are three possible structures for PCl_2F_3 with phosphorus as the central atom. Draw them and discuss how measurements of dipole moments could help distinguish among them.

Exercise:**Problem:**

Describe the molecular structure around the indicated atom or atoms:

(a) the sulfur atom in sulfuric acid, H_2SO_4 [$(\text{HO})_2\text{SO}_2$]

(b) the chlorine atom in chloric acid, HClO_3 [HOClO_2]

(c) the oxygen atom in hydrogen peroxide, HOOH

(d) the nitrogen atom in nitric acid, HNO_3 [HONO_2]

- (e) the oxygen atom in the OH group in nitric acid, HNO_3 [HONO_2]
 - (f) the central oxygen atom in the ozone molecule, O_3
 - (g) each of the carbon atoms in propyne, CH_3CCH
 - (h) the carbon atom in Freon, CCl_2F_2
 - (i) each of the carbon atoms in allene, H_2CCCH_2
-

Solution:

- (a) tetrahedral; (b) trigonal pyramidal; (c) bent (109°); (d) trigonal planar;
 (e) bent (109°); (f) bent (109°); (g) $\underline{\text{C}}\text{H}_3\text{CCH}$ tetrahedral, $\text{CH}_3\underline{\text{C}}\underline{\text{C}}\text{H}$ linear;
 (h) tetrahedral; (i) $\text{H}_2\underline{\text{C}}\underline{\text{C}}\text{CH}_2$ linear; $\text{H}_2\underline{\text{C}}\underline{\text{C}}\underline{\text{C}}\text{H}_2$ trigonal planar

Exercise:

Problem:

Draw the Lewis structures and predict the shape of each compound or ion:

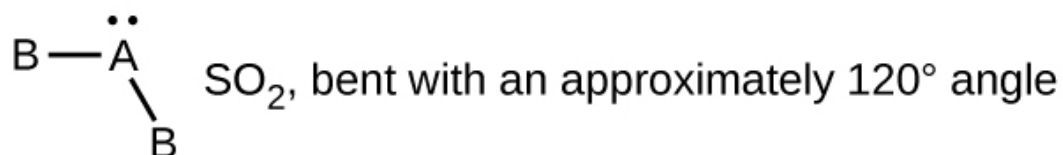
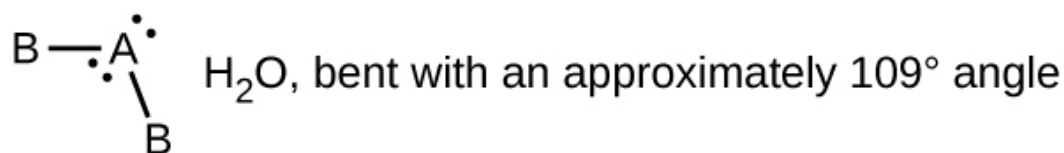
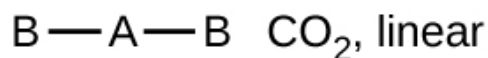
- (a) CO_2
- (b) NO_2^-
- (c) SO_3
- (d) SO_3^{2-}

Exercise:

Problem:

A molecule with the formula AB_2 , in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion for each shape.

Solution:



Exercise:

Problem:

A molecule with the formula AB_3 , in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion that has each shape.

Exercise:

Problem:

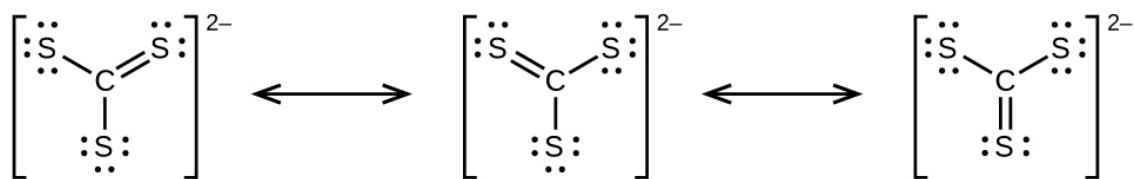
Draw the Lewis electron dot structures for these molecules, including resonance structures where appropriate:



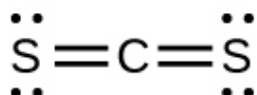
(d) predict the molecular shapes for CS_3^{2-} and CS_2 and explain how you arrived at your predictions

Solution:

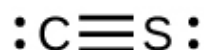
(a)



;
(b)



;
(c)



;
(d) CS_3^{2-} includes three regions of electron density (all are bonds with no lone pairs); the shape is trigonal planar; CS_2 has only two regions of electron density (all bonds with no lone pairs); the shape is linear

Exercise:

Problem:

What is the molecular structure of the stable form of FNO_2 ? (N is the central atom.)

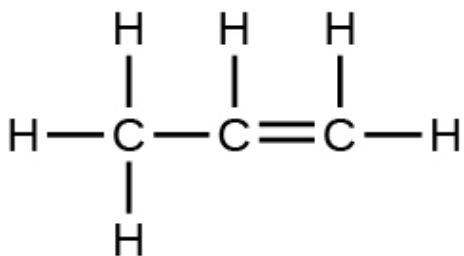
Exercise:

Problem:

A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen. What is its molecular structure?

Solution:

The Lewis structure is made from three units, but the atoms must be rearranged:



Exercise:

Problem:

Use the [simulation](#) to perform the following exercises for a two-atom molecule:

- (a) Adjust the electronegativity value so the bond dipole is pointing toward B. Then determine what the electronegativity values must be to switch the dipole so that it points toward A.
- (b) With a partial positive charge on A, turn on the electric field and describe what happens.
- (c) With a small partial negative charge on A, turn on the electric field and describe what happens.
- (d) Reset all, and then with a large partial negative charge on A, turn on the electric field and describe what happens.

Exercise:

Problem:

Use the [simulation](#) to perform the following exercises for a real molecule. You may need to rotate the molecules in three dimensions to see certain dipoles.

- (a) Sketch the bond dipoles and molecular dipole (if any) for O₃. Explain your observations.
- (b) Look at the bond dipoles for NH₃. Use these dipoles to predict whether N or H is more electronegative.

(c) Predict whether there should be a molecular dipole for NH_3 and, if so, in which direction it will point. Check the molecular dipole box to test your hypothesis.

Solution:

The molecular dipole points away from the hydrogen atoms.

Exercise:

Problem:

Use the [Molecule Shape simulator](#) to build a molecule. Starting with the central atom, click on the double bond to add one double bond. Then add one single bond and one lone pair. Rotate the molecule to observe the complete geometry. Name the electron group geometry and molecular structure and predict the bond angle. Then click the check boxes at the bottom and right of the simulator to check your answers.

Exercise:

Problem:

Use the [Molecule Shape simulator](#) to explore real molecules. On the Real Molecules tab, select H_2O . Switch between the “real” and “model” modes. Explain the difference observed.

Solution:

The structures are very similar. In the model mode, each electron group occupies the same amount of space, so the bond angle is shown as 109.5° . In the “real” mode, the lone pairs are larger, causing the hydrogens to be compressed. This leads to the smaller angle of 104.5° .

Exercise:

Problem:

Use the [Molecule Shape simulator](#) to explore real molecules. On the Real Molecules tab, select “model” mode and S_2O . What is the model bond angle? Explain whether the “real” bond angle should be larger or smaller than the ideal model angle.

Glossary

axial position

location in a trigonal bipyramidal geometry in which there is another atom at a 180° angle and the equatorial positions are at a 90° angle

bond angle

angle between any two covalent bonds that share a common atom

bond distance

(also, bond length) distance between the nuclei of two bonded atoms

bond dipole moment

separation of charge in a bond that depends on the difference in electronegativity and the bond distance represented by partial charges or a vector

dipole moment

property of a molecule that describes the separation of charge determined by the sum of the individual bond moments based on the molecular structure

electron-pair geometry

arrangement around a central atom of all regions of electron density (bonds, lone pairs, or unpaired electrons)

equatorial position

one of the three positions in a trigonal bipyramidal geometry with 120° angles between them; the axial positions are located at a 90° angle

linear

shape in which two outside groups are placed on opposite sides of a central atom

molecular structure

structure that includes only the placement of the atoms in the molecule

octahedral

shape in which six outside groups are placed around a central atom such that a three-dimensional shape is generated with four groups forming a

square and the other two forming the apex of two pyramids, one above and one below the square plane

polar molecule

(also, dipole) molecule with an overall dipole moment

tetrahedral

shape in which four outside groups are placed around a central atom such that a three-dimensional shape is generated with four corners and 109.5° angles between each pair and the central atom

trigonal bipyramidal

shape in which five outside groups are placed around a central atom such that three form a flat triangle with 120° angles between each pair and the central atom, and the other two form the apex of two pyramids, one above and one below the triangular plane

trigonal planar

shape in which three outside groups are placed in a flat triangle around a central atom with 120° angles between each pair and the central atom

valence shell electron-pair repulsion theory (VSEPR)

theory used to predict the bond angles in a molecule based on positioning regions of high electron density as far apart as possible to minimize electrostatic repulsion

vector

quantity having magnitude and direction

Introduction

class="introduction"

- Energy Basics
- Calorimetry
- Enthalpy

Sliding a
match head
along a
rough
surface
initiates a
combustion
reaction that
produces
energy in
the form of
heat and
light.
(credit:
modificatio
n of work
by Laszlo
Ilyes)



Chemical reactions, such as those that occur when you light a match, involve changes in energy as well as matter. Societies at all levels of development could not function without the energy released by chemical reactions. In 2012, about 85% of US energy consumption came from the combustion of petroleum products, coal, wood, and garbage. We use this energy to produce electricity (38%); to transport food, raw materials, manufactured goods, and people (27%); for industrial production (21%); and to heat and power our homes and businesses (10%).[\[footnote\]](#) While these combustion reactions help us meet our essential energy needs, they are also recognized by the majority of the scientific community as a major contributor to global climate change.

US Energy Information Administration, *Primary Energy Consumption by Source and Sector*, 2012,

http://www.eia.gov/totalenergy/data/monthly/pdf/flow/css_2012_energy.pdf
. Data derived from US Energy Information Administration, *Monthly Energy Review* (January 2014).

Useful forms of energy are also available from a variety of chemical reactions other than combustion. For example, the energy produced by the batteries in a cell phone, car, or flashlight results from chemical reactions. This chapter introduces many of the basic ideas necessary to explore the relationships between chemical changes and energy, with a focus on thermal energy.

Energy Basics

By the end of this section, you will be able to:

- Define energy, distinguish types of energy, and describe the nature of energy changes that accompany chemical and physical changes
- Distinguish the related properties of heat, thermal energy, and temperature
- Define and distinguish specific heat and heat capacity, and describe the physical implications of both
- Perform calculations involving heat, specific heat, and temperature change

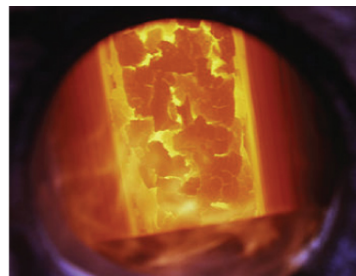
Chemical changes and their accompanying changes in energy are important parts of our everyday world ([\[link\]](#)). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We burn a variety of fuels (gasoline, natural gas, coal) to produce energy for transportation, heating, and the generation of electricity. Industrial chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cars, skyscrapers, and bridges.



(a)



(b)



(c)

The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. (credit a: modification of work by

“Pink Sherbet Photography”/Flickr; credit b: modification of work by Jeffery Turner)

Over 90% of the energy we use comes originally from the sun. Every day, the sun provides the earth with almost 10,000 times the amount of energy necessary to meet all of the world’s energy needs for that day. Our challenge is to find ways to convert and store incoming solar energy so that it can be used in reactions or chemical processes that are both convenient and nonpolluting. Plants and many bacteria capture solar energy through photosynthesis. We release the energy stored in plants when we burn wood or plant products such as ethanol. We also use this energy to fuel our bodies by eating food that comes directly from plants or from animals that got their energy by eating plants. Burning coal and petroleum also releases stored solar energy: These fuels are fossilized plant and animal matter.

This chapter will introduce the basic ideas of an important area of science concerned with the amount of heat absorbed or released during chemical and physical changes—an area called **thermochemistry**. The concepts introduced in this chapter are widely used in almost all scientific and technical fields. Food scientists use them to determine the energy content of foods. Biologists study the energetics of living organisms, such as the metabolic combustion of sugar into carbon dioxide and water. The oil, gas, and transportation industries, renewable energy providers, and many others endeavor to find better methods to produce energy for our commercial and personal needs. Engineers strive to improve energy efficiency, find better ways to heat and cool our homes, refrigerate our food and drinks, and meet the energy and cooling needs of computers and electronics, among other applications. Understanding thermochemical principles is essential for chemists, physicists, biologists, geologists, every type of engineer, and just about anyone who studies or does any kind of science.

Energy

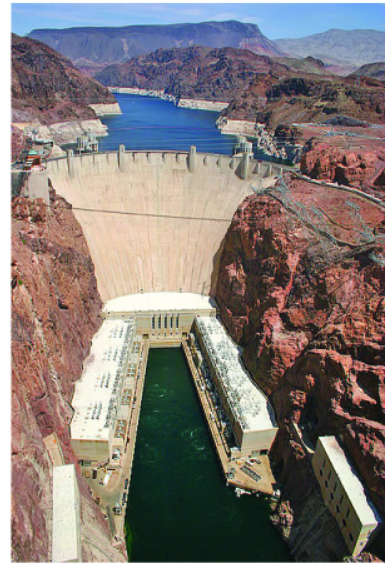
Energy can be defined as the capacity to supply heat or do work. One type of **work (w)** is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move

matter (the air in the pump) against the opposing force of the air already in the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: **potential energy**, the energy an object has because of its relative position, composition, or condition, and **kinetic energy**, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant ([link](#)). A battery has potential energy because the chemicals within it can produce electricity that can do work.



(a)



(b)

(a) Water that is higher in elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by “curimedia”/Wikimedia commons)

Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the law of conservation of energy: during a chemical or physical change, energy can be neither created nor destroyed, although it can be changed in form. (This is also one version of the first law of thermodynamics, as you will learn later.)

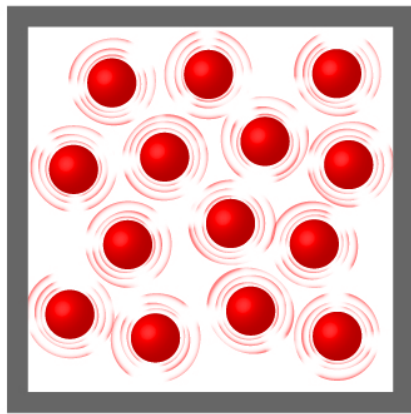
When one substance is converted into another, there is always an associated conversion of one form of energy into another. Heat is usually released or absorbed, but sometimes the conversion involves light, electrical energy, or some other form of energy. For example, chemical energy (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is combusted within the cylinders of a car's engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders' pistons.

According to the law of conservation of matter (seen in an earlier chapter), there is no detectable change in the total amount of matter during a chemical change. When chemical reactions occur, the energy changes are relatively modest and the mass changes are too small to measure, so the laws of conservation of matter and energy hold well. However, in nuclear reactions, the energy changes are much larger (by factors of a million or so), the mass changes are measurable, and matter-energy conversions are significant. This will be examined in more detail in a later chapter on nuclear chemistry. To encompass both chemical and nuclear changes, we combine these laws into one statement: The total quantity of matter and energy in the universe is fixed.

Thermal Energy, Temperature, and Heat

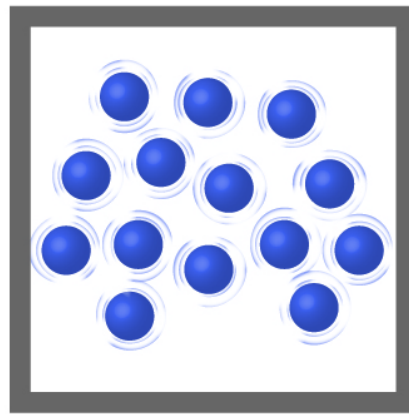
Thermal energy is kinetic energy associated with the random motion of atoms and molecules. **Temperature** is a quantitative measure of “hot” or “cold.” When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the

object is “hot.” When the atoms and molecules are moving slowly, they have lower average KE, and we say that the object is “cold” ([\[link\]](#)). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.



Hot water

(a)



Cold water

(b)

(a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

Note:

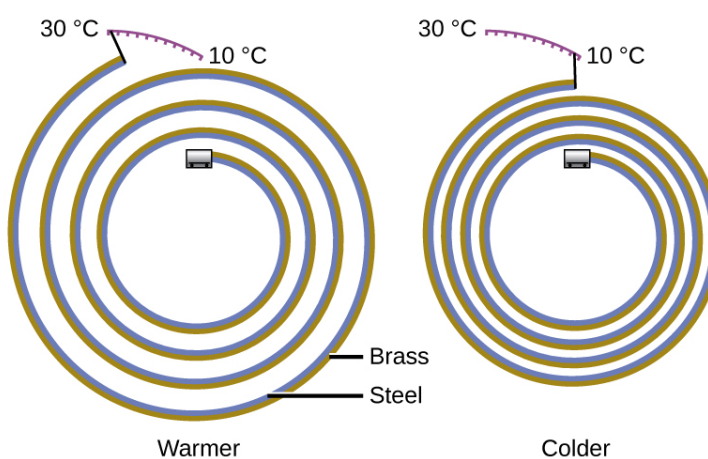


Click on this [interactive simulation](#) to view the effects of temperature on molecular motion.

Most substances expand as their temperature increases and contract as their temperature decreases. This property can be used to measure temperature changes, as shown in [\[link\]](#). The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.



(a)



(b)

(a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. When heated or cooled, one of the metals (brass)

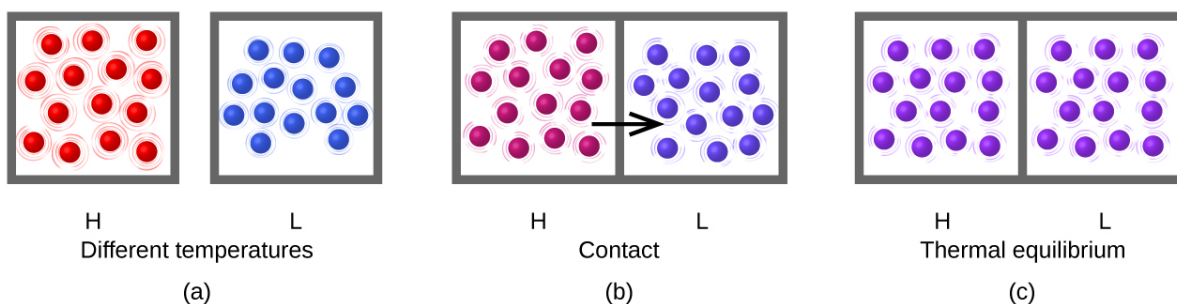
expands or contracts more than the other metal (steel), causing the strip to coil or uncoil. Both types of thermometers have a calibrated scale that indicates the temperature. (credit a: modification of work by “dwstucke”/Flickr)

Note:



The following [demonstration](#) allows one to view the effects of heating and cooling a coiled bimetallic strip.

Heat (q) is the transfer of thermal energy between two bodies at different temperatures. Heat flow (a redundant term, but one commonly used) increases the thermal energy of one body and decreases the thermal energy of the other. Suppose we initially have a high temperature (and high thermal energy) substance (H) and a low temperature (and low thermal energy) substance (L). The atoms and molecules in H have a higher average KE than those in L. If we place substance H in contact with substance L, the thermal energy will flow spontaneously from substance H to substance L. The temperature of substance H will decrease, as will the average KE of its molecules; the temperature of substance L will increase, along with the average KE of its molecules. Heat flow will continue until the two substances are at the same temperature ([\[link\]](#)).



(a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they are put into contact with each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach “thermal equilibrium” when both substances are at the same temperature, and their molecules have the same average kinetic energy.

Note:



Click on the [PhET simulation](#) to explore energy forms and changes. Visit the Energy Systems tab to create combinations of energy sources, transformation methods, and outputs. Click on Energy Symbols to visualize the transfer of energy.

Matter undergoing chemical reactions and physical changes can release or absorb heat. A change that releases heat is called an **exothermic process**.

For example, the combustion reaction that occurs when using an oxyacetylene torch is an exothermic process—this process also releases energy in the form of light as evidenced by the torch's flame ([link](#)). A reaction or change that absorbs heat is an **endothermic process**. A cold pack used to treat muscle strains provides an example of an endothermic process. When the substances in the cold pack (water and a salt like ammonium nitrate) are brought together, the resulting process absorbs heat, leading to the sensation of cold.



(a)



(b)

(a) An oxyacetylene torch produces heat by the combustion of acetylene in oxygen. The energy released by this exothermic reaction heats and then melts the metal being cut. The sparks are tiny bits of the molten metal flying away. (b) A cold pack uses an endothermic process to create the sensation of cold. (credit a: modification of work by “Skatebiker”/Wikimedia commons)

Historically, energy was measured in units of **calories (cal)**. A calorie is the amount of energy required to raise one gram of water by 1 degree C (1 kelvin). However, this quantity depends on the atmospheric pressure and the starting temperature of the water. The ease of measurement of energy changes in calories has meant that the calorie is still frequently used. The

Calorie (with a capital C), or large calorie, commonly used in quantifying food energy content, is a kilocalorie. The SI unit of heat, work, and energy is the joule. A **joule (J)** is defined as the amount of energy used when a force of 1 newton moves an object 1 meter. It is named in honor of the English physicist James Prescott Joule. One joule is equivalent to 1 kg m²/s², which is also called 1 newton–meter. A kilojoule (kJ) is 1000 joules. To standardize its definition, 1 calorie has been set to equal 4.184 joules.

We now introduce two concepts useful in describing heat flow and temperature change. The **heat capacity (C)** of a body of matter is the quantity of heat (q) it absorbs or releases when it experiences a temperature change (ΔT) of 1 degree Celsius (or equivalently, 1 kelvin):

Equation:

$$C = \frac{q}{\Delta T}$$

Heat capacity is determined by both the type and amount of substance that absorbs or releases heat. It is therefore an extensive property—its value is proportional to the amount of the substance.

For example, consider the heat capacities of two cast iron frying pans. The heat capacity of the large pan is five times greater than that of the small pan because, although both are made of the same material, the mass of the large pan is five times greater than the mass of the small pan. More mass means more atoms are present in the larger pan, so it takes more energy to make all of those atoms vibrate faster. The heat capacity of the small cast iron frying pan is found by observing that it takes 18,150 J of energy to raise the temperature of the pan by 50.0 °C:

Equation:

$$C_{\text{small pan}} = \frac{18,140 \text{ J}}{50.0 \text{ }^{\circ}\text{C}} = 363 \text{ J}/^{\circ}\text{C}$$

The larger cast iron frying pan, while made of the same substance, requires 90,700 J of energy to raise its temperature by 50.0 °C. The larger pan has a

(proportionally) larger heat capacity because the larger amount of material requires a (proportionally) larger amount of energy to yield the same temperature change:

Equation:

$$C_{\text{large pan}} = \frac{90,700 \text{ J}}{50.0 \text{ }^{\circ}\text{C}} = 1814 \text{ J/}^{\circ}\text{C}$$

The **specific heat capacity (*c*)** of a substance, commonly called its “specific heat,” is the quantity of heat required to raise the temperature of 1 gram of a substance by 1 degree Celsius (or 1 kelvin):

Equation:

$$c = \frac{q}{m\Delta T}$$

Specific heat capacity depends only on the kind of substance absorbing or releasing heat. It is an intensive property—the type, but not the amount, of the substance is all that matters. For example, the small cast iron frying pan has a mass of 808 g. The specific heat of iron (the material used to make the pan) is therefore:

Equation:

$$c_{\text{iron}} = \frac{18,140 \text{ J}}{(808 \text{ g})(50.0 \text{ }^{\circ}\text{C})} = 0.449 \text{ J/g }^{\circ}\text{C}$$

The large frying pan has a mass of 4040 g. Using the data for this pan, we can also calculate the specific heat of iron:

Equation:

$$c_{\text{iron}} = \frac{90,700 \text{ J}}{(4040 \text{ g})(50.0 \text{ }^{\circ}\text{C})} = 0.449 \text{ J/g }^{\circ}\text{C}$$

Although the large pan is more massive than the small pan, since both are made of the same material, they both yield the same value for specific heat

(for the material of construction, iron). Note that specific heat is measured in units of energy per temperature per mass and is an intensive property, being derived from a ratio of two extensive properties (heat and mass). The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and has units of $\text{J/mol } ^\circ\text{C}$ ([link](#)).



Due to its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (credit: Mark Blaser)

Liquid water has a relatively high specific heat (about $4.2 \text{ J/g } ^\circ\text{C}$); most metals have much lower specific heats (usually less than $1 \text{ J/g } ^\circ\text{C}$). The specific heat of a substance varies somewhat with temperature. However, this variation is usually small enough that we will treat specific heat as constant over the range of temperatures that will be considered in this chapter. Specific heats of some common substances are listed in [link](#).

Specific Heats of Common Substances at 25 °C and 1 bar		
Substance	Symbol (<i>state</i>)	Specific Heat (J/g °C)
helium	He(<i>g</i>)	5.193
water	H ₂ O(<i>l</i>)	4.184
ethanol	C ₂ H ₆ O(<i>l</i>)	2.376
ice	H ₂ O(<i>s</i>)	2.093 (at −10 °C)
water vapor	H ₂ O(<i>g</i>)	1.864
nitrogen	N ₂ (<i>g</i>)	1.040
air		1.007
oxygen	O ₂ (<i>g</i>)	0.918
aluminum	Al(<i>s</i>)	0.897
carbon dioxide	CO ₂ (<i>g</i>)	0.853
argon	Ar(<i>g</i>)	0.522
iron	Fe(<i>s</i>)	0.449
copper	Cu(<i>s</i>)	0.385
lead	Pb(<i>s</i>)	0.130
gold	Au(<i>s</i>)	0.129
silicon	Si(<i>s</i>)	0.712

If we know the mass of a substance and its specific heat, we can determine the amount of heat, q , entering or leaving the substance by measuring the temperature change before and after the heat is gained or lost:

Equation:

$$q = (\text{specific heat}) \times (\text{mass of substance}) \times (\text{temperature change})$$
$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

In this equation, c is the specific heat of the substance, m is its mass, and ΔT (which is read “delta T”) is the temperature change, $T_{\text{final}} - T_{\text{initial}}$. If a substance gains thermal energy, its temperature increases, its final temperature is higher than its initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a positive value, and the value of q is positive. If a substance loses thermal energy, its temperature decreases, the final temperature is lower than the initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a negative value, and the value of q is negative.

Example:

Measuring Heat

A flask containing 8.0×10^2 g of water is heated, and the temperature of the water increases from 21 °C to 85 °C. How much heat did the water absorb?

Solution

To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case, 8.0×10^2 g)
- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C, so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need *800 times as much* to heat 8.0×10^2 g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water

by 1 °C, we will need *64 times as much* to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using the equation:

Equation:

$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

Equation:

$$\begin{aligned} &= (4.184 \text{ J/g } ^\circ\text{C}) \times (8.0 \times 10^2 \text{ g}) \times (85 - 21) ^\circ\text{C} \\ &= (4.184 \text{ J/g } ^\circ\text{C}) \times (8.0 \times 10^2 \text{ g}) \times (64) ^\circ\text{C} \\ &= 210,000 \text{ J } (= 2.1 \times 10^5 \text{ kJ}) \end{aligned}$$

Because the temperature increased, the water absorbed heat and q is positive.

Check Your Learning

How much heat, in joules, must be added to a $5.07 \times 10^4 \text{ g}$ iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.449 J/g °C.

Note:

Answer:

$$5.07 \times 10^4 \text{ J}$$

Note that the relationship between heat, specific heat, mass, and temperature change can be used to determine any of these quantities (not just heat) if the other three are known or can be deduced.

Example:**Determining Other Quantities**

A piece of unknown metal weighs 348 g. When the metal piece absorbs 6.64 kJ of heat, its temperature increases from 22.4 °C to 43.6 °C.

Determine the specific heat of this metal (which might provide a clue to its identity).

Solution

Since mass, heat, and temperature change are known for this metal, we can determine its specific heat using the relationship:

Equation:

$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

Substituting the known values:

Equation:

$$6640 \text{ J} = c \times (348 \text{ g}) \times (43.6 - 22.4) ^\circ\text{C}$$

Solving:

Equation:

$$c = \frac{6640 \text{ J}}{(348 \text{ g}) \times (21.2 ^\circ\text{C})} = 0.900 \text{ J/g } ^\circ\text{C}$$

Comparing this value with the values in [\[link\]](#), this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

Check Your Learning

A piece of unknown metal weighs 217 g. When the metal piece absorbs 1.43 kJ of heat, its temperature increases from 24.5 °C to 39.1 °C.

Determine the specific heat of this metal, and predict its identity.

Note:**Answer:**

$c = 0.451 \text{ J/g } ^\circ\text{C}$; the metal is likely to be iron

Note:

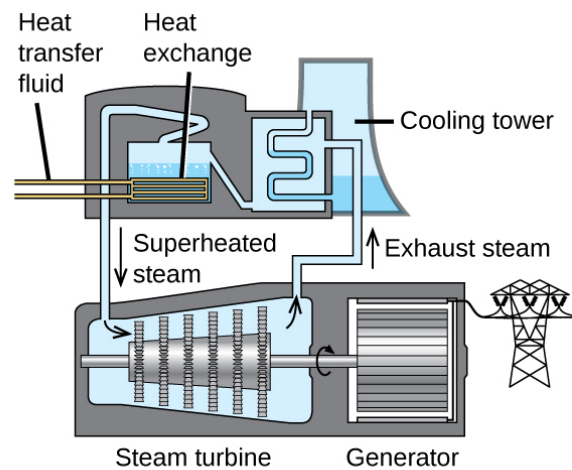
Solar Thermal Energy Power Plants

The sunlight that reaches the earth contains thousands of times more energy than we presently capture. Solar thermal systems provide one possible solution to the problem of converting energy from the sun into energy we can use. Large-scale solar thermal plants have different design specifics, but all concentrate sunlight to heat some substance; the heat “stored” in that substance is then converted into electricity.

The Solana Generating Station in Arizona’s Sonora Desert produces 280 megawatts of electrical power. It uses parabolic mirrors that focus sunlight on pipes filled with a heat transfer fluid (HTF) ([link](#)). The HTF then does two things: It turns water into steam, which spins turbines, which in turn produces electricity, and it melts and heats a mixture of salts, which functions as a thermal energy storage system. After the sun goes down, the molten salt mixture can then release enough of its stored heat to produce steam to run the turbines for 6 hours. Molten salts are used because they possess a number of beneficial properties, including high heat capacities and thermal conductivities.



(a)



(b)

This solar thermal plant uses parabolic trough mirrors to concentrate sunlight. (credit a: modification of work by Bureau of Land

Management)

The 377-megawatt Ivanpah Solar Generating System, located in the Mojave Desert in California, is the largest solar thermal power plant in the world ([\[link\]](#)). Its 170,000 mirrors focus huge amounts of sunlight on three water-filled towers, producing steam at over 538 °C that drives electricity-producing turbines. It produces enough energy to power 140,000 homes. Water is used as the working fluid because of its large heat capacity and heat of vaporization.



(a)



(b)

(a) The Ivanpah solar thermal plant uses 170,000 mirrors to concentrate sunlight on water-filled towers. (b) It covers 4000 acres of public land near the Mojave Desert and the California-Nevada border.

(credit a: modification of work by Craig Dietrich; credit b: modification of work by “USFWS Pacific Southwest Region”/Flickr)

Key Concepts and Summary

Energy is the capacity to do work (applying a force to move matter). Kinetic energy (KE) is the energy of motion; potential energy is energy due to relative position, composition, or condition. When energy is converted

from one form into another, energy is neither created nor destroyed (law of conservation of energy or first law of thermodynamics).

Matter has thermal energy due to the KE of its molecules and temperature that corresponds to the average KE of its molecules. Heat is energy that is transferred between objects at different temperatures; it flows from a high to a low temperature. Chemical and physical processes can absorb heat (endothermic) or release heat (exothermic). The SI unit of energy, heat, and work is the joule (J).

Specific heat and heat capacity are measures of the energy needed to change the temperature of a substance or object. The amount of heat absorbed or released by a substance depends directly on the type of substance, its mass, and the temperature change it undergoes.

Key Equations

- $q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$

Chemistry End of Chapter Exercises

Exercise:

Problem:

A burning match and a bonfire may have the same temperature, yet you would not sit around a burning match on a fall evening to stay warm. Why not?

Solution:

The temperature of 1 gram of burning wood is approximately the same for both a match and a bonfire. This is an intensive property and depends on the material (wood). However, the overall amount of produced heat depends on the amount of material; this is an extensive property. The amount of wood in a bonfire is much greater than that in a match; the total amount of produced heat is also much greater, which

is why we can sit around a bonfire to stay warm, but a match would not provide enough heat to keep us from getting cold.

Exercise:

Problem:

Prepare a table identifying several energy transitions that take place during the typical operation of an automobile.

Exercise:

Problem:

Explain the difference between heat capacity and specific heat of a substance.

Solution:

Heat capacity refers to the heat required to raise the temperature of the mass of the substance 1 degree; specific heat refers to the heat required to raise the temperature of 1 gram of the substance 1 degree. Thus, heat capacity is an extensive property, and specific heat is an intensive one.

Exercise:

Problem:

Calculate the heat capacity, in joules and in calories per degree, of the following:

(a) 28.4 g of water

(b) 1.00 oz of lead

Exercise:

Problem:

Calculate the heat capacity, in joules and in calories per degree, of the following:

(a) 45.8 g of nitrogen gas

(b) 1.00 pound of aluminum metal

Solution:

(a) 47.6 J/°C; 11.38 cal °C⁻¹; (b) 407 J/°C; 97.3 cal °C⁻¹

Exercise:

Problem:

How much heat, in joules and in calories, must be added to a 75.0-g iron block with a specific heat of 0.449 J/g °C to increase its temperature from 25 °C to its melting temperature of 1535 °C?

Exercise:

Problem:

How much heat, in joules and in calories, is required to heat a 28.4-g (1-oz) ice cube from -23.0 °C to -1.0 °C?

Solution:

1310 J; 313 cal

Exercise:

Problem:

How much would the temperature of 275 g of water increase if 36.5 kJ of heat were added?

Exercise:

Problem:

If 14.5 kJ of heat were added to 485 g of liquid water, how much would its temperature increase?

Solution:

7.15 °C

Exercise:

Problem:

A piece of unknown substance weighs 44.7 g and requires 2110 J to increase its temperature from 23.2 °C to 89.6 °C.

- (a) What is the specific heat of the substance?
- (b) If it is one of the substances found in [\[link\]](#), what is its likely identity?

Exercise:

Problem:

A piece of unknown solid substance weighs 437.2 g, and requires 8460 J to increase its temperature from 19.3 °C to 68.9 °C.

- (a) What is the specific heat of the substance?
- (b) If it is one of the substances found in [\[link\]](#), what is its likely identity?

Solution:

- (a) 0.390 J/g °C; (b) Copper is a likely candidate.

Exercise:

Problem: An aluminum kettle weighs 1.05 kg.

- (a) What is the heat capacity of the kettle?
- (b) How much heat is required to increase the temperature of this kettle from 23.0 °C to 99.0 °C?
- (c) How much heat is required to heat this kettle from 23.0 °C to 99.0 °C if it contains 1.25 L of water (density of 0.997 g/mL and a specific

heat of 4.184 J/g °C)?

Exercise:

Problem:

Most people find waterbeds uncomfortable unless the water temperature is maintained at about 85 °F. Unless it is heated, a waterbed that contains 892 L of water cools from 85 °F to 72 °F in 24 hours. Estimate the amount of electrical energy required over 24 hours, in kWh, to keep the bed from cooling. Note that 1 kilowatt-hour (kWh) = 3.6×10^6 J, and assume that the density of water is 1.0 g/mL (independent of temperature). What other assumptions did you make? How did they affect your calculated result (i.e., were they likely to yield “positive” or “negative” errors)?

Solution:

We assume that the density of water is 1.0 g/cm³(1 g/mL) and that it takes as much energy to keep the water at 85 °F as to heat it from 72 °F to 85 °F. We also assume that only the water is going to be heated.
Energy required = 7.47 kWh

Glossary

calorie (cal)

unit of heat or other energy; the amount of energy required to raise 1 gram of water by 1 degree Celsius; 1 cal is defined as 4.184 J

endothermic process

chemical reaction or physical change that absorbs heat

energy

capacity to supply heat or do work

exothermic process

chemical reaction or physical change that releases heat

heat (q)

transfer of thermal energy between two bodies

heat capacity (C)

extensive property of a body of matter that represents the quantity of heat required to increase its temperature by 1 degree Celsius (or 1 kelvin)

joule (J)

SI unit of energy; 1 joule is the kinetic energy of an object with a mass of 2 kilograms moving with a velocity of 1 meter per second, $1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2$ and $4.184 \text{ J} = 1 \text{ cal}$

kinetic energy

energy of a moving body, in joules, equal to $\frac{1}{2}mv^2$ (where m = mass and v = velocity)

potential energy

energy of a particle or system of particles derived from relative position, composition, or condition

specific heat capacity (c)

intensive property of a substance that represents the quantity of heat required to raise the temperature of 1 gram of the substance by 1 degree Celsius (or 1 kelvin)

temperature

intensive property of matter that is a quantitative measure of “hotness” and “coldness”

thermal energy

kinetic energy associated with the random motion of atoms and molecules

thermochemistry

study of measuring the amount of heat absorbed or released during a chemical reaction or a physical change

work (w)

energy transfer due to changes in external, macroscopic variables such as pressure and volume; or causing matter to move against an opposing force

Introduction

class="introduction"

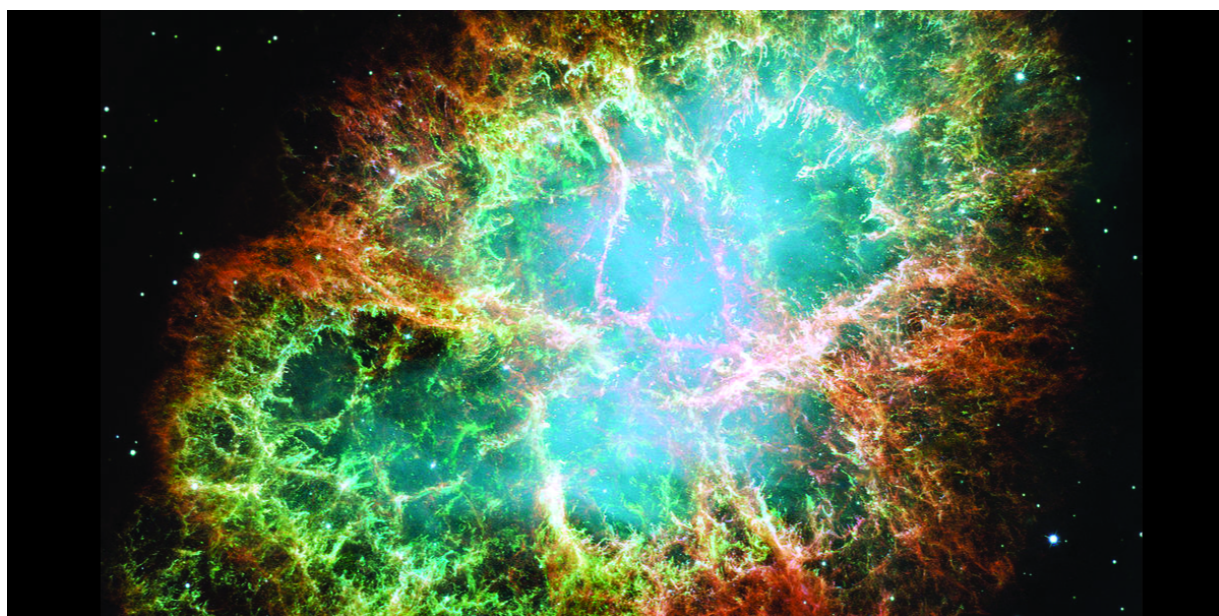
- Electromagnetic Energy
- The Bohr Model
- Development of Quantum Theory
- Electronic Structure of Atoms (Electron Configurations)
- Periodic Variations in Element Properties

The Crab
Nebula
consists of
remnants of a
supernova
(the explosion
of a star).

NASA's
Hubble Space
Telescope
produced this
composite
image.

Measurements of the
emitted light
wavelengths
enabled
astronomers
to identify the
elements in
the nebula,
determining
that it
contains
specific ions
including S^+

(green
filaments) and
 O^{2+} (red
filaments).
(credit:
modification
of work by
NASA and
ESA)



In 1054, Chinese astronomers recorded the appearance of a “guest star” in the sky, visible even during the day, which then disappeared slowly over the next two years. The sudden appearance was due to a supernova explosion, which was much brighter than the original star. Even though this supernova was observed almost a millennium ago, the remaining Crab Nebula ([\[link\]](#)) continues to release energy today. It emits not only visible light but also infrared light, X-rays, and other forms of electromagnetic radiation. The nebula emits both continuous spectra (the blue-white glow) and atomic emission spectra (the colored filaments). In this chapter, we will discuss light and other forms of electromagnetic radiation and how they are related to the electronic structure of atoms. We will also see how this radiation can be used to identify elements, even from thousands of light years away.

Electromagnetic Energy

By the end of this section, you will be able to:

- Explain the basic behavior of waves, including travelling waves and standing waves
- Describe the wave nature of light
- Use appropriate equations to calculate related light-wave properties such as frequency, wavelength, and energy
- Distinguish between line and continuous emission spectra
- Describe the particle nature of light

The nature of light has been a subject of inquiry since antiquity. In the seventeenth century, Isaac Newton performed experiments with lenses and prisms and was able to demonstrate that white light consists of the individual colors of the rainbow combined together. Newton explained his optics findings in terms of a "corpuscular" view of light, in which light was composed of streams of extremely tiny particles travelling at high speeds according to Newton's laws of motion. Others in the seventeenth century, such as Christiaan Huygens, had shown that optical phenomena such as reflection and refraction could be equally well explained in terms of light as waves travelling at high speed through a medium called "luminiferous aether" that was thought to permeate all space. Early in the nineteenth century, Thomas Young demonstrated that light passing through narrow, closely spaced slits produced interference patterns that could not be explained in terms of Newtonian particles but could be easily explained in terms of waves. Later in the nineteenth century, after James Clerk Maxwell developed his theory of **electromagnetic radiation** and showed that light was the visible part of a vast spectrum of electromagnetic waves, the particle view of light became thoroughly discredited. By the end of the nineteenth century, scientists viewed the physical universe as roughly comprising two separate domains: matter composed of particles moving according to Newton's laws of motion, and electromagnetic radiation consisting of waves governed by Maxwell's equations. Today, these domains are referred to as classical mechanics and classical electrodynamics (or classical electromagnetism). Although there were a few physical phenomena that could not be explained within this framework, scientists at that time were so confident of the overall soundness of this

framework that they viewed these aberrations as puzzling paradoxes that would ultimately be resolved somehow within this framework. As we shall see, these paradoxes led to a contemporary framework that intimately connects particles and waves at a fundamental level called wave-particle duality, which has superseded the classical view.

Visible light and other forms of electromagnetic radiation play important roles in chemistry, since they can be used to infer the energies of electrons within atoms and molecules. Much of modern technology is based on electromagnetic radiation. For example, radio waves from a mobile phone, X-rays used by dentists, the energy used to cook food in your microwave, the radiant heat from red-hot objects, and the light from your television screen are forms of electromagnetic radiation that all exhibit wavelike behavior.

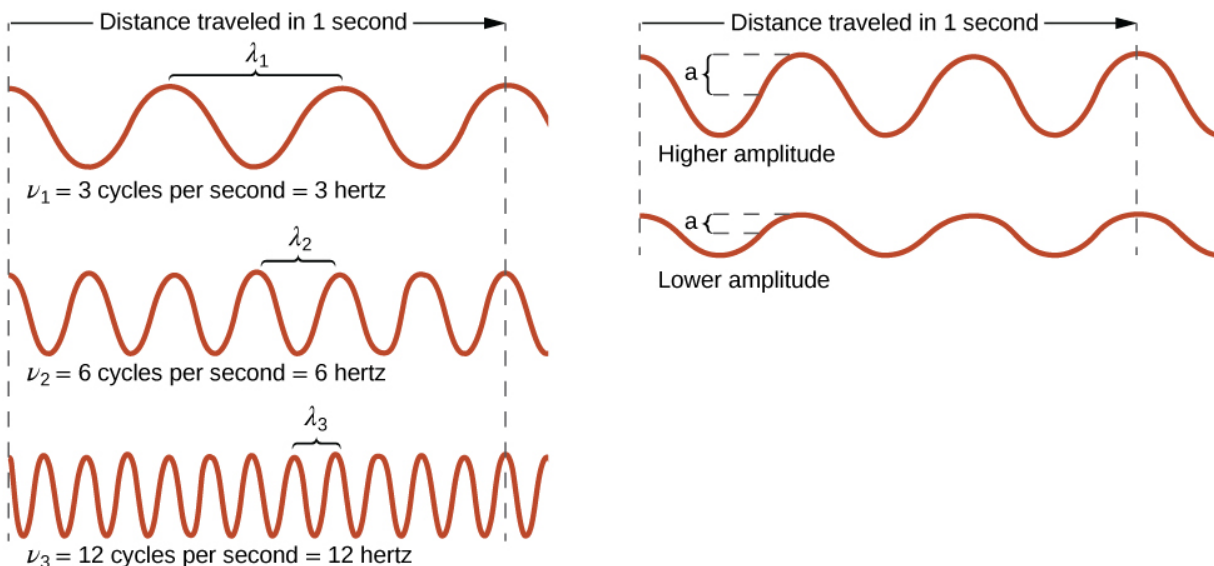
Waves

A **wave** is an oscillation or periodic movement that can transport energy from one point in space to another. Common examples of waves are all around us. Shaking the end of a rope transfers energy from your hand to the other end of the rope, dropping a pebble into a pond causes waves to ripple outward along the water's surface, and the expansion of air that accompanies a lightning strike generates sound waves (thunder) that can travel outward for several miles. In each of these cases, kinetic energy is transferred through matter (the rope, water, or air) while the matter remains essentially in place. An insightful example of a wave occurs in sports stadiums when fans in a narrow region of seats rise simultaneously and stand with their arms raised up for a few seconds before sitting down again while the fans in neighboring sections likewise stand up and sit down in sequence. While this wave can quickly encircle a large stadium in a few seconds, none of the fans actually travel with the wave—they all stay in or above their seats.

Waves need not be restricted to travel through matter. As Maxwell showed, electromagnetic waves consist of an electric field oscillating in step with a perpendicular magnetic field, both of which are perpendicular to the

direction of travel. These waves can travel through a vacuum at a constant speed of 2.998×10^8 m/s, the speed of light (denoted by c).

All waves, including forms of electromagnetic radiation, are characterized by, a **wavelength** (denoted by λ , the lowercase Greek letter lambda), a **frequency** (denoted by ν , the lowercase Greek letter nu), and an **amplitude**. As can be seen in [\[link\]](#), the wavelength is the distance between two consecutive peaks or troughs in a wave (measured in meters in the SI system). Electromagnetic waves have wavelengths that fall within an enormous range-wavelengths of kilometers (10^3 m) to picometers (10^{-12} m) have been observed. The frequency is the number of wave cycles that pass a specified point in space in a specified amount of time (in the SI system, this is measured in seconds). A cycle corresponds to one complete wavelength. The unit for frequency, expressed as cycles per second [s^{-1}], is the **hertz (Hz)**. Common multiples of this unit are megahertz, ($1 \text{ MHz} = 1 \times 10^6 \text{ Hz}$) and gigahertz ($1 \text{ GHz} = 1 \times 10^9 \text{ Hz}$). The amplitude corresponds to the magnitude of the wave's displacement and so, in [\[link\]](#), this corresponds to one-half the height between the peaks and troughs. The amplitude is related to the intensity of the wave, which for light is the brightness, and for sound is the loudness.



One-dimensional sinusoidal waves show the relationship among

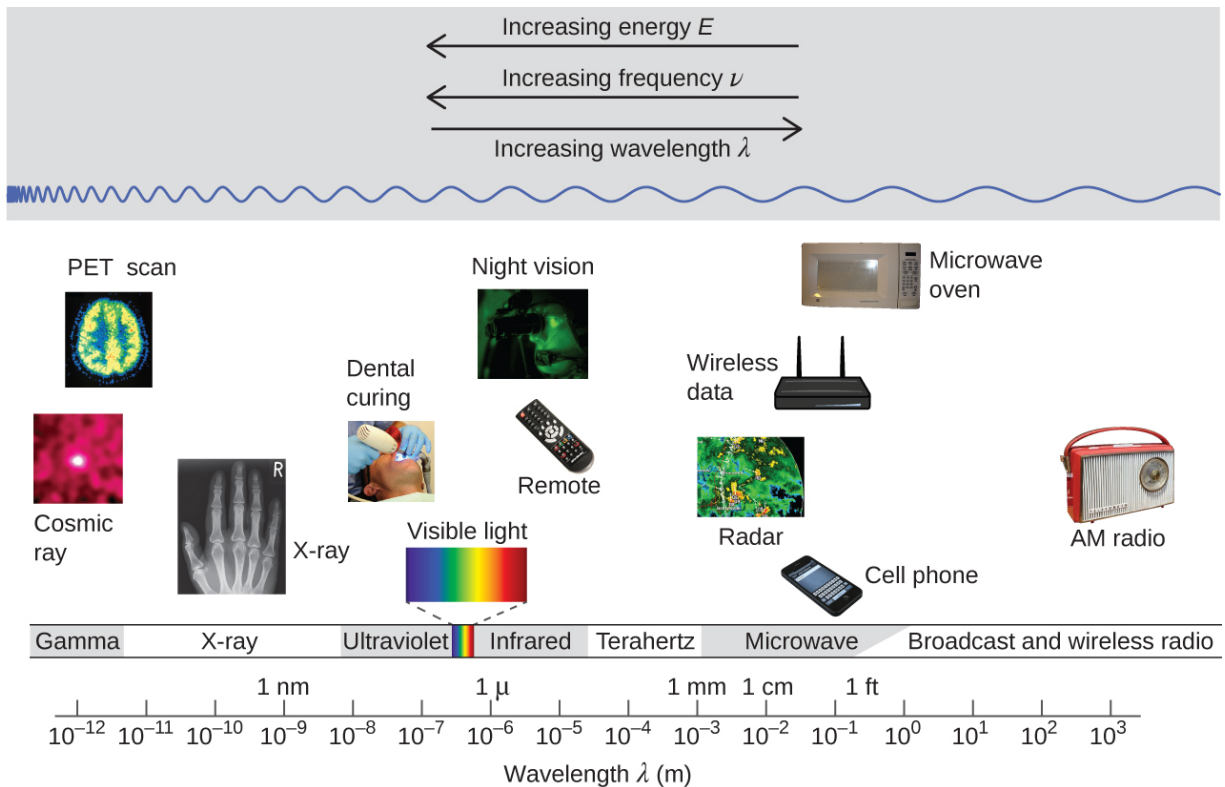
wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough.

The product of a wave's wavelength (λ) and its frequency (ν), $\lambda\nu$, is the speed of the wave. Thus, for electromagnetic radiation in a vacuum:

Equation:

$$c = 2.998 \times 10^8 \text{ms}^{-1} = \lambda\nu$$

Wavelength and frequency are inversely proportional: As the wavelength increases, the frequency decreases. The inverse proportionality is illustrated in [\[link\]](#). This figure also shows the **electromagnetic spectrum**, the range of all types of electromagnetic radiation. Each of the various colors of visible light has specific frequencies and wavelengths associated with them, and you can see that visible light makes up only a small portion of the electromagnetic spectrum. Because the technologies developed to work in various parts of the electromagnetic spectrum are different, for reasons of convenience and historical legacies, different units are typically used for different parts of the spectrum. For example, radio waves are usually specified as frequencies (typically in units of MHz), while the visible region is usually specified in wavelengths (typically in units of nm or angstroms).



Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength. Examples of some applications for various wavelengths include positron emission tomography (PET) scans, X-ray imaging, remote controls, wireless Internet, cellular telephones, and radios. (credit “Cosmic ray”: modification of work by NASA; credit “PET scan”: modification of work by the National Institute of Health; credit “X-ray”: modification of work by Dr. Jochen Lengerke; credit “Dental curing”: modification of work by the Department of the Navy; credit “Night vision”: modification of work by the Department of the Army; credit “Remote”: modification of work by Emilian Robert Vicol; credit “Cell phone”: modification of work by Brett Jordan; credit “Microwave oven”: modification of work by Billy Mabray; credit “Ultrasound”: modification of work by Jane Whitney; credit “AM radio”: modification of work by Dave Clausen)

Example:**Determining the Frequency and Wavelength of Radiation**

A sodium streetlight gives off yellow light that has a wavelength of 589 nm ($1 \text{ nm} = 1 \times 10^{-9} \text{ m}$). What is the frequency of this light?

Solution

We can rearrange the equation $c = \lambda\nu$ to solve for the frequency:

Equation:

$$\nu = \frac{c}{\lambda}$$

Since c is expressed in meters per second, we must also convert 589 nm to meters.

Equation:

$$\nu = \left(\frac{2.998 \times 10^8 \cancel{\text{m}} \text{s}^{-1}}{589 \cancel{\text{nm}}} \right) \left(\frac{1 \times 10^9 \cancel{\text{nm}}}{1 \cancel{\text{m}}} \right) = 5.09 \times 10^{14} \text{s}^{-1}$$

Check Your Learning

One of the frequencies used to transmit and receive cellular telephone signals in the United States is 850 MHz. What is the wavelength in meters of these radio waves?

Note:**Answer:**

$$0.353 \text{ m} = 35.3 \text{ cm}$$

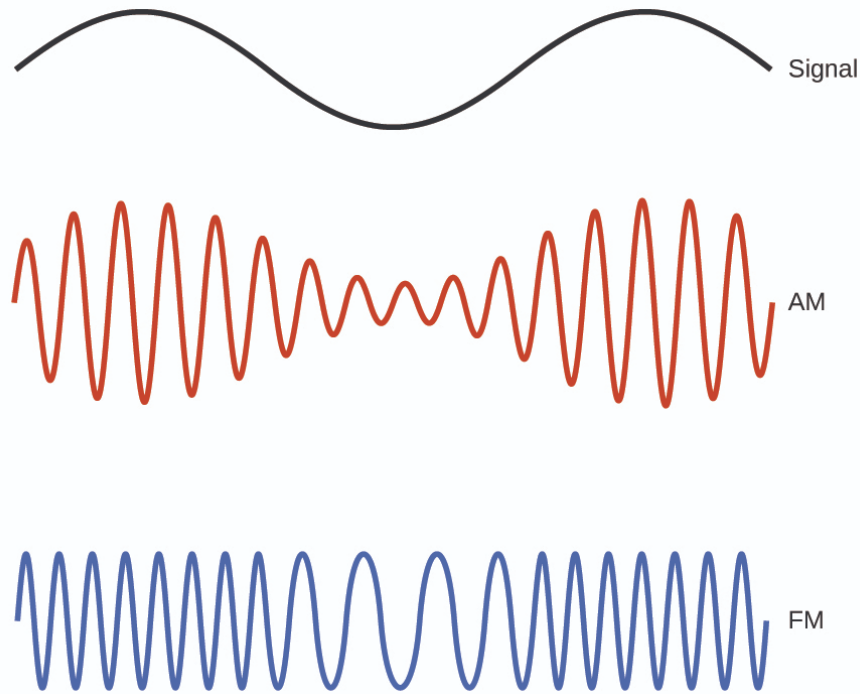
Note:

Wireless Communication



Radio and cell towers are typically used to transmit long-wavelength electromagnetic radiation. Increasingly, cell towers are designed to blend in with the landscape, as with the Tucson, Arizona, cell tower (right) disguised as a palm tree. (credit left: modification of work by Sir Mildred Pierce; credit middle: modification of work by M.O. Stevens)

Many valuable technologies operate in the radio (3 kHz-300 GHz) frequency region of the electromagnetic spectrum. At the low frequency (low energy, long wavelength) end of this region are AM (amplitude modulation) radio signals (540-2830 kHz) that can travel long distances. FM (frequency modulation) radio signals are used at higher frequencies (87.5-108.0 MHz). In AM radio, the information is transmitted by varying the amplitude of the wave ([link](#)). In FM radio, by contrast, the amplitude is constant and the instantaneous frequency varies.

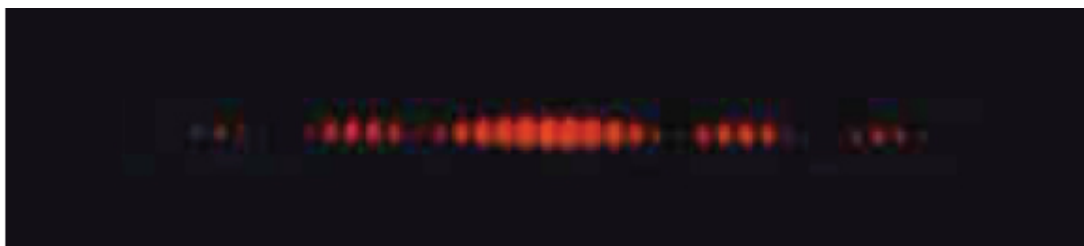


This schematic depicts how amplitude modulation (AM) and frequency modulation (FM) can be used to transmit a radio wave.

Other technologies also operate in the radio-wave portion of the electromagnetic spectrum. For example, 4G cellular telephone signals are approximately 880 MHz, while Global Positioning System (GPS) signals operate at 1.228 and 1.575 GHz, local area wireless technology (Wi-Fi) networks operate at 2.4 to 5 GHz, and highway toll sensors operate at 5.8 GHz. The frequencies associated with these applications are convenient because such waves tend not to be absorbed much by common building materials.

One particularly characteristic phenomenon of waves results when two or more waves come into contact: They interfere with each other. [\[link\]](#) shows the **interference patterns** that arise when light passes through narrow slits closely spaced about a wavelength apart. The fringe patterns produced depend on the wavelength, with the fringes being more closely spaced for shorter wavelength light passing through a given set of slits. When the light

passes through the two slits, each slit effectively acts as a new source, resulting in two closely spaced waves coming into contact at the detector (the camera in this case). The dark regions in [\[link\]](#) correspond to regions where the peaks for the wave from one slit happen to coincide with the troughs for the wave from the other slit (destructive interference), while the brightest regions correspond to the regions where the peaks for the two waves (or their two troughs) happen to coincide (constructive interference). Likewise, when two stones are tossed close together into a pond, interference patterns are visible in the interactions between the waves produced by the stones. Such interference patterns cannot be explained by particles moving according to the laws of classical mechanics.



Interference fringe patterns are shown for light passing through two closely spaced, narrow slits. The spacing of the fringes depends on the wavelength, with the fringes being more closely spaced for the shorter-wavelength blue light. (credit: PASCO)

Note:

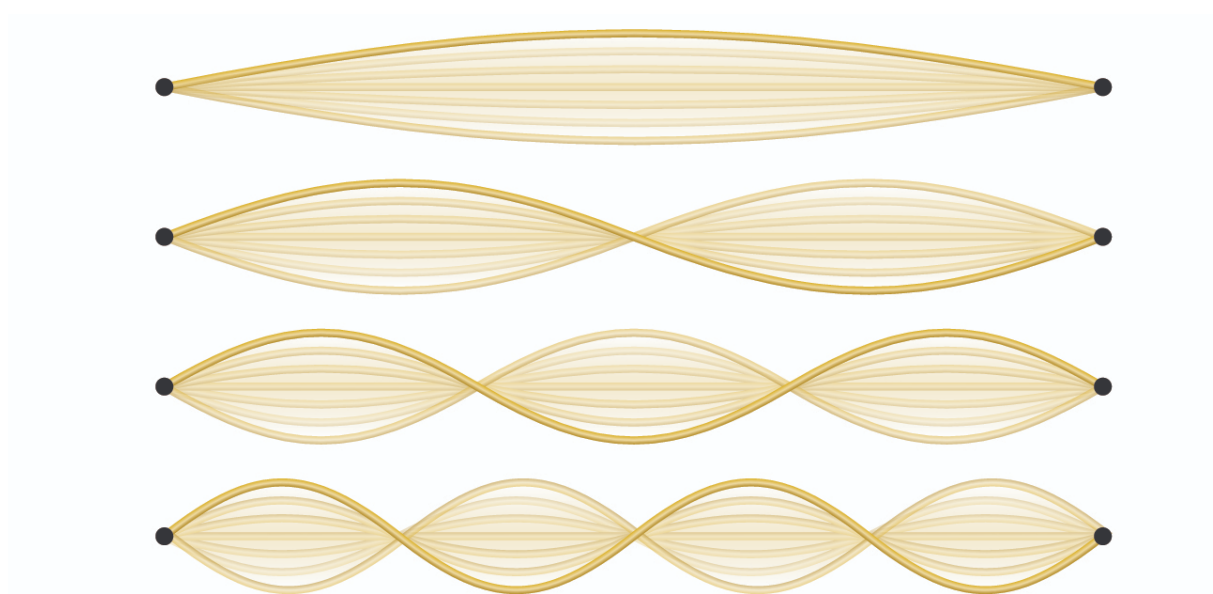
Dorothy Hodgkin

Because the wavelengths of X-rays (10-10,000 picometers [pm]) are comparable to the size of atoms, X-rays can be used to determine the structure of molecules. When a beam of X-rays is passed through molecules packed together in a crystal, the X-rays collide with the electrons and scatter. Constructive and destructive interference of these scattered X-rays creates a specific diffraction pattern. Calculating

backward from this pattern, the positions of each of the atoms in the molecule can be determined very precisely. One of the pioneers who helped create this technology was Dorothy Crowfoot Hodgkin. She was born in Cairo, Egypt, in 1910, where her British parents were studying archeology. Even as a young girl, she was fascinated with minerals and crystals. When she was a student at Oxford University, she began researching how X-ray crystallography could be used to determine the structure of biomolecules. She invented new techniques that allowed her and her students to determine the structures of vitamin B₁₂, penicillin, and many other important molecules. Diabetes, a disease that affects 382 million people worldwide, involves the hormone insulin. Hodgkin began studying the structure of insulin in 1934, but it required several decades of advances in the field before she finally reported the structure in 1969. Understanding the structure has led to better understanding of the disease and treatment options.

Not all waves are travelling waves. **Standing waves** (also known as **stationary waves**) remain constrained within some region of space. As we shall see, standing waves play an important role in our understanding of the electronic structure of atoms and molecules. The simplest example of a standing wave is a one-dimensional wave associated with a vibrating string that is held fixed at its two end points. [\[link\]](#) shows the four lowest-energy standing waves (the fundamental wave and the lowest three harmonics) for a vibrating string at a particular amplitude. Although the string's motion lies mostly within a plane, the wave itself is considered to be one dimensional, since it lies along the length of the string. The motion of string segments in a direction perpendicular to the string length generates the waves and so the amplitude of the waves is visible as the maximum displacement of the curves seen in [\[link\]](#). The key observation from the figure is *that only those waves having an integer number, n , of half-wavelengths between the end points can form*. A system with fixed end points such as this restricts the number and type of the possible waveforms. This is an example of **quantization**, in which only discrete values from a more general set of continuous values of some property are observed. Another important observation is that the harmonic waves (those waves displaying more than

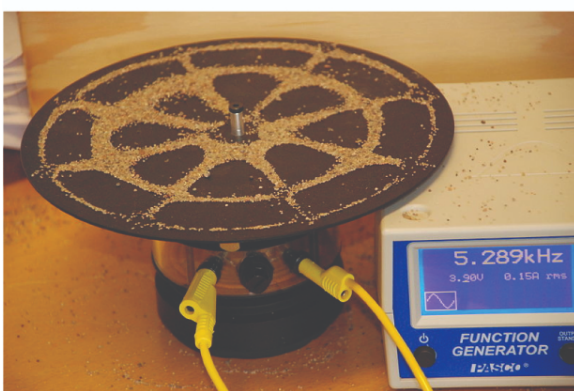
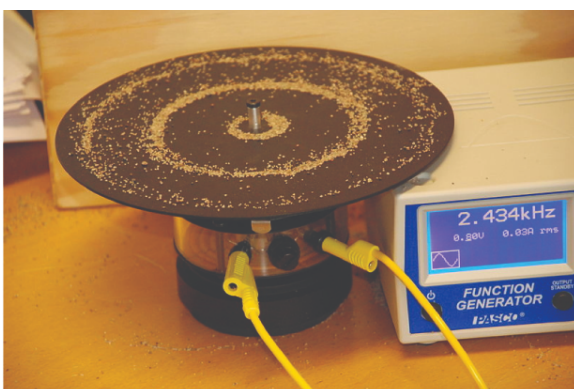
one-half wavelength) all have one or more points between the two end points that are not in motion. These special points are **nodes**. The energies of the standing waves with a given amplitude in a vibrating string increase with the number of half-wavelengths n . Since the number of nodes is $n - 1$, the energy can also be said to depend on the number of nodes, generally increasing as the number of nodes increases.



A vibrating string shows some one-dimensional standing waves. Since the two end points of the string are held fixed, only waves having an integer number of half-wavelengths can form. The points on the string between the end points that are not moving are called the nodes.

An example of two-dimensional standing waves is shown in [\[link\]](#), which shows the vibrational patterns on a flat surface. Although the vibrational amplitudes cannot be seen like they could in the vibrating string, the nodes have been made visible by sprinkling the drum surface with a powder that collects on the areas of the surface that have minimal displacement. For one-dimensional standing waves, the nodes were points on the line, but for two-dimensional standing waves, the nodes are lines on the surface (for

three-dimensional standing waves, the nodes are two-dimensional surfaces within the three-dimensional volume). Because of the circular symmetry of the drum surface, its boundary conditions (the drum surface being tightly constrained to the circumference of the drum) result in two types of nodes: radial nodes that sweep out all angles at constant radii and, thus, are seen as circles about the center, and angular nodes that sweep out all radii at constant angles and, thus, are seen as lines passing through the center. The upper left image in [\[link\]](#) shows two radial nodes, while the image in the lower right shows the vibrational pattern associated with three radial nodes and two angular nodes.



Two-dimensional standing waves can be visualized on a vibrating surface. The surface has been sprinkled with a powder that collects near the nodal lines. There are two types of nodes visible: radial nodes (circles) and angular nodes (radii).

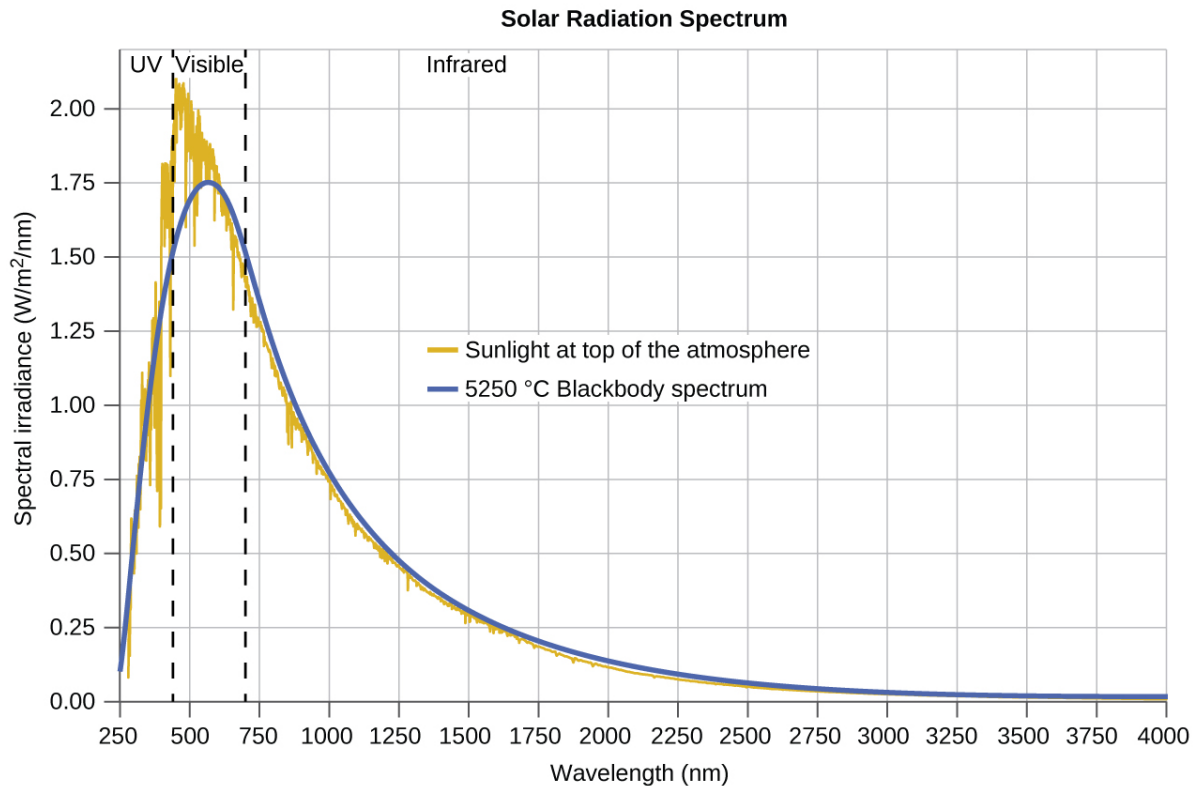
Note:



You can watch the formation of various radial nodes [here](#) as singer Imogen Heap projects her voice across a kettle drum.

Blackbody Radiation and the Ultraviolet Catastrophe

The last few decades of the nineteenth century witnessed intense research activity in commercializing newly discovered electric lighting. This required obtaining a better understanding of the distributions of light emitted from various sources being considered. Artificial lighting is usually designed to mimic natural sunlight within the limitations of the underlying technology. Such lighting consists of a range of broadly distributed frequencies that form a **continuous spectrum**. [\[link\]](#) shows the wavelength distribution for sunlight. The most intense radiation is in the visible region, with the intensity dropping off rapidly for shorter wavelength ultraviolet (UV) light, and more slowly for longer wavelength infrared (IR) light.



The spectral distribution (light intensity vs. wavelength) of sunlight reaches the Earth's atmosphere as UV light, visible light, and IR light. The unabsorbed sunlight at the top of the atmosphere has a distribution that approximately matches the theoretical distribution of a blackbody at 5250 °C, represented by the blue curve. (credit: modification of work by American Society for Testing and Materials (ASTM) Terrestrial Reference Spectra for Photovoltaic Performance Evaluation)

In [\[link\]](#), the solar distribution is compared to a representative distribution, called a blackbody spectrum, that corresponds to a temperature of 5250 °C. The blackbody spectrum matches the solar spectrum quite well. A **blackbody** is a convenient, ideal emitter that approximates the behavior of many materials when heated. It is “ideal” in the same sense that an ideal gas is a convenient, simple representation of real gases that works well, provided that the pressure is not too high nor the temperature too low. A good approximation of a blackbody that can be used to observe blackbody

radiation is a metal oven that can be heated to very high temperatures. The oven has a small hole allowing for the light being emitted within the oven to be observed with a spectrometer so that the wavelengths and their intensities can be measured. [\[link\]](#) shows the resulting curves for some representative temperatures. Each distribution depends only on a single parameter: the temperature. The maxima in the blackbody curves, λ_{max} , shift to shorter wavelengths as the temperature increases, reflecting the observation that metals being heated to high temperatures begin to glow a darker red that becomes brighter as the temperature increases, eventually becoming white hot at very high temperatures as the intensities of all of the visible wavelengths become appreciable. This common observation was at the heart of the first paradox that showed the fundamental limitations of classical physics that we will examine.

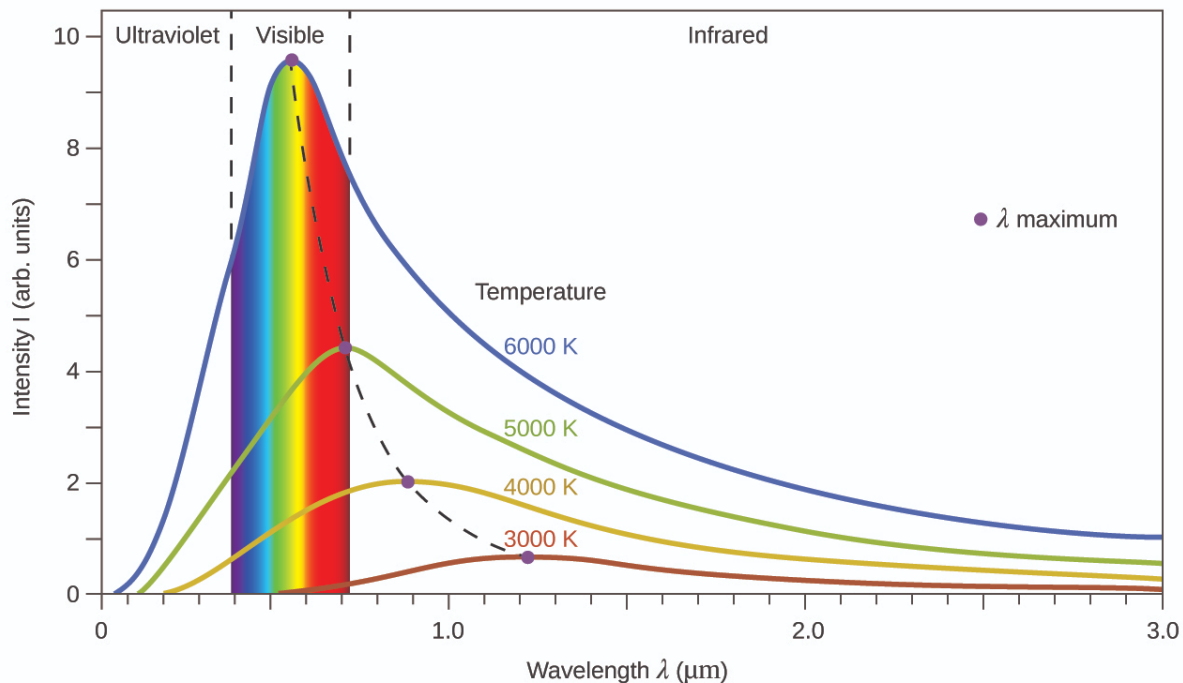
Physicists derived mathematical expressions for the blackbody curves using well-accepted concepts from the theories of classical mechanics and classical electromagnetism. The theoretical expressions as functions of temperature fit the observed experimental blackbody curves well at longer wavelengths, but showed significant discrepancies at shorter wavelengths. Not only did the theoretical curves not show a peak, they absurdly showed the intensity becoming infinitely large as the wavelength became smaller, which would imply that everyday objects at room temperature should be emitting large amounts of UV light. This became known as the “ultraviolet catastrophe” because no one could find any problems with the theoretical treatment that could lead to such unrealistic short-wavelength behavior. Finally, around 1900, Max Planck derived a theoretical expression for blackbody radiation that fit the experimental observations exactly (within experimental error). Planck developed his theoretical treatment by extending the earlier work that had been based on the premise that the atoms composing the oven vibrated at increasing frequencies (or decreasing wavelengths) as the temperature increased, with these vibrations being the source of the emitted electromagnetic radiation. But where the earlier treatments had allowed the vibrating atoms to have any energy values obtained from a continuous set of energies (perfectly reasonable, according to classical physics), Planck found that by restricting the vibrational energies to discrete values for each frequency, he could derive an

expression for blackbody radiation that correctly had the intensity dropping rapidly for the short wavelengths in the UV region.

Equation:

$$E = nh\nu, n = 1, 2, 3, \dots$$

The quantity h is a constant now known as Planck's constant, in his honor. Although Planck was pleased he had resolved the blackbody radiation paradox, he was disturbed that to do so, he needed to assume the vibrating atoms required quantized energies, which he was unable to explain. The value of Planck's constant is very small, 6.626×10^{-34} joule seconds (J s), which helps explain why energy quantization had not been observed previously in macroscopic phenomena.



Blackbody spectral distribution curves are shown for some representative temperatures.

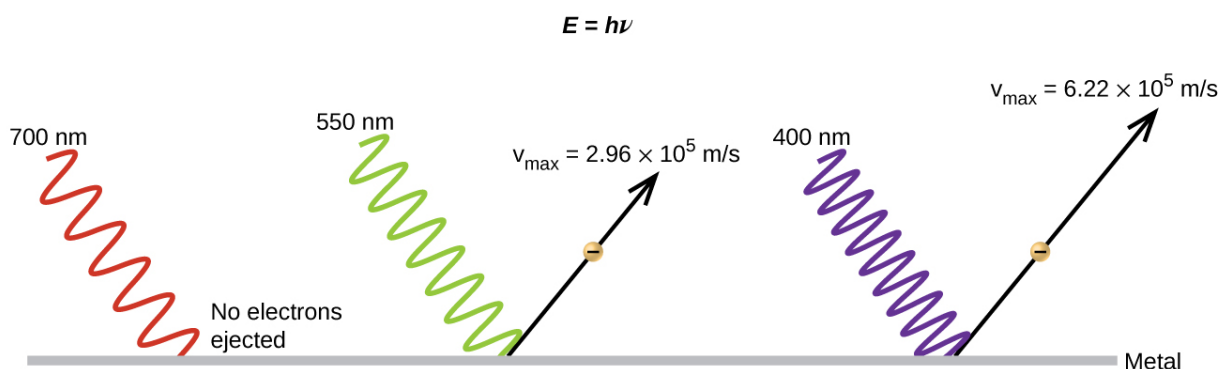
The Photoelectric Effect

The next paradox in the classical theory to be resolved concerned the photoelectric effect ([link](#)). It had been observed that electrons could be ejected from the clean surface of a metal when light having a frequency greater than some threshold frequency was shone on it. Surprisingly, the kinetic energy of the ejected electrons did not depend on the brightness of the light, but increased with increasing frequency of the light. Since the electrons in the metal had a certain amount of binding energy keeping them there, the incident light needed to have more energy to free the electrons. According to classical wave theory, a wave's energy depends on its intensity (which depends on its amplitude), not its frequency. One part of these observations was that the number of electrons ejected within a given time period was seen to increase as the brightness increased. In 1905, Albert Einstein was able to resolve the paradox by incorporating Planck's quantization findings into the discredited particle view of light (Einstein actually won his Nobel prize for this work, and not for his theories of relativity for which he is most famous).

Einstein argued that the quantized energies that Planck had postulated in his treatment of blackbody radiation could be applied to the light in the photoelectric effect so that the light striking the metal surface should not be viewed as a wave, but instead as a stream of particles (later called **photons**) whose energy depended on their frequency, according to Planck's formula, $E = h\nu$ (or, in terms of wavelength using $c = \nu\lambda$, $E = \frac{hc}{\lambda}$). Electrons were ejected when hit by photons having sufficient energy (a frequency greater than the threshold). The greater the frequency, the greater the kinetic energy imparted to the escaping electrons by the collisions. Einstein also argued that the light intensity did not depend on the amplitude of the incoming wave, but instead corresponded to the number of photons striking the surface within a given time period. This explains why the number of ejected electrons increased with increasing brightness, since the greater the number of incoming photons, the greater the likelihood that they would collide with some of the electrons.

With Einstein's findings, the nature of light took on a new air of mystery. Although many light phenomena could be explained either in terms of

waves or particles, certain phenomena, such as the interference patterns obtained when light passed through a double slit, were completely contrary to a particle view of light, while other phenomena, such as the photoelectric effect, were completely contrary to a wave view of light. Somehow, at a deep fundamental level still not fully understood, light is both wavelike and particle-like. This is known as **wave-particle duality**.



Photons with low frequencies do not have enough energy to cause electrons to be ejected via the photoelectric effect. For any frequency of light above the threshold frequency, the kinetic energy of an ejected electron will increase linearly with the energy of the incoming photon.

Example:

Calculating the Energy of Radiation

When we see light from a neon sign, we are observing radiation from excited neon atoms. If this radiation has a wavelength of 640 nm, what is the energy of the photon being emitted?

Solution

We use the part of Planck's equation that includes the wavelength, λ , and convert units of nanometers to meters so that the units of λ and c are the same.

Equation:

$$E = \frac{hc}{\lambda}$$

Equation:

$$E = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1})}{(640\text{-nm})\left(\frac{1\text{ m}}{10^9\text{-nm}}\right)}$$

$$E = 3.10 \times 10^{-19} \text{ J}$$

Check Your Learning

The microwaves in an oven are of a specific frequency that will heat the water molecules contained in food. (This is why most plastics and glass do not become hot in a microwave oven—they do not contain water molecules.) This frequency is about 3×10^9 Hz. What is the energy of one photon in these microwaves?

Note:

Answer:

$$2 \times 10^{-24} \text{ J}$$

Note:



Use this [simulation program](#) to experiment with the photoelectric effect to see how intensity, frequency, type of metal, and other factors influence the ejected photons.

Example:

Photoelectric Effect

Identify which of the following statements are false and, where necessary, change the italicized word or phrase to make them true, consistent with Einstein's explanation of the photoelectric effect.

- (a) Increasing the brightness of incoming light *increases* the kinetic energy of the ejected electrons.
- (b) Increasing the *wavelength* of incoming light increases the kinetic energy of the ejected electrons.
- (c) Increasing the brightness of incoming light *increases* the number of ejected electrons.
- (d) Increasing the *frequency* of incoming light can increase the number of ejected electrons.

Solution

- (a) False. Increasing the brightness of incoming light *has no effect* on the kinetic energy of the ejected electrons. Only energy, not the number or amplitude, of the photons influences the kinetic energy of the electrons.
- (b) False. Increasing the *frequency* of incoming light increases the kinetic energy of the ejected electrons. Frequency is proportional to energy and inversely proportional to wavelength. Frequencies above the threshold value transfer the excess energy into the kinetic energy of the electrons.
- (c) True. Because the number of collisions with photons increases with brighter light, the number of ejected electrons increases.
- (d) True with regard to the threshold energy binding the electrons to the metal. Below this threshold, electrons are not emitted and above it they are. Once over the threshold value, further increasing the frequency does not increase the number of ejected electrons

Check Your Learning

Calculate the threshold energy in kJ/mol of electrons in aluminum, given that the lowest frequency photon for which the photoelectric effect is observed is 9.87×10^{14} Hz.

Note:

Answer:

394 kJ/mol

Line Spectra

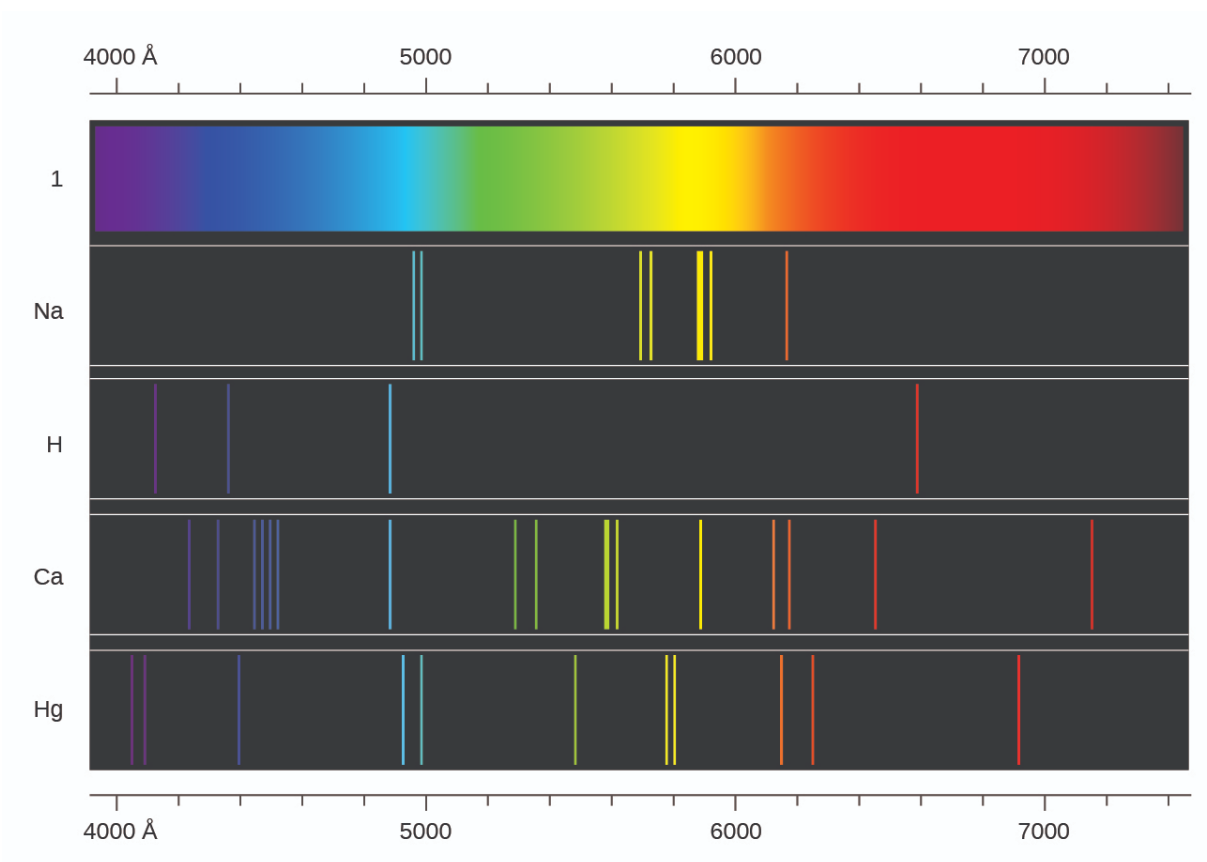
Another paradox within the classical electromagnetic theory that scientists in the late nineteenth century struggled with concerned the light emitted from atoms and molecules. When solids, liquids, or condensed gases are heated sufficiently, they radiate some of the excess energy as light. Photons produced in this manner have a range of energies, and thereby produce a continuous spectrum in which an unbroken series of wavelengths is present. Most of the light generated from stars (including our sun) is produced in this fashion. You can see all the visible wavelengths of light present in sunlight by using a prism to separate them. As can be seen in [\[link\]](#), sunlight also contains UV light (shorter wavelengths) and IR light (longer wavelengths) that can be detected using instruments but that are invisible to the human eye. Incandescent (glowing) solids such as tungsten filaments in incandescent lights also give off light that contains all wavelengths of visible light. These continuous spectra can often be approximated by blackbody radiation curves at some appropriate temperature, such as those shown in [\[link\]](#).

In contrast to continuous spectra, light can also occur as discrete or **line spectra** having very narrow line widths interspersed throughout the spectral regions such as those shown in [\[link\]](#). Exciting a gas at low partial pressure using an electrical current, or heating it, will produce line spectra. Fluorescent light bulbs and neon signs operate in this way ([\[link\]](#)). Each element displays its own characteristic set of lines, as do molecules, although their spectra are generally much more complicated.



Neon signs operate by exciting a gas at low partial pressure using an electrical current. This sign shows the elaborate artistic effects that can be achieved. (credit: Dave Shaver)

Each emission line consists of a single wavelength of light, which implies that the light emitted by a gas consists of a set of discrete energies. For example, when an electric discharge passes through a tube containing hydrogen gas at low pressure, the H_2 molecules are broken apart into separate H atoms and we see a blue-pink color. Passing the light through a prism produces a line spectrum, indicating that this light is composed of photons of four visible wavelengths, as shown in [\[link\]](#).



Compare the two types of emission spectra: continuous spectrum of white light (top) and the line spectra of the light from excited sodium, hydrogen, calcium, and mercury atoms.

The origin of discrete spectra in atoms and molecules was extremely puzzling to scientists in the late nineteenth century, since according to classical electromagnetic theory, only continuous spectra should be observed. Even more puzzling, in 1885, Johann Balmer was able to derive an empirical equation that related the four visible wavelengths of light emitted by hydrogen atoms to whole integers. That equation is the following one, in which k is a constant:

Equation:

$$\frac{1}{\lambda} = k \left(\frac{1}{4} - \frac{1}{n^2} \right), n = 3, 4, 5, 6$$

Other discrete lines for the hydrogen atom were found in the UV and IR regions. Johannes Rydberg generalized Balmer's work and developed an empirical formula that predicted all of hydrogen's emission lines, not just those restricted to the visible range, where, n_1 and n_2 are integers, $n_1 < n_2$, and R_∞ is the Rydberg constant ($1.097 \times 10^7 \text{ m}^{-1}$).

Equation:

$$\frac{1}{\lambda} = R_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Even in the late nineteenth century, spectroscopy was a very precise science, and so the wavelengths of hydrogen were measured to very high accuracy, which implied that the Rydberg constant could be determined very precisely as well. That such a simple formula as the Rydberg formula could account for such precise measurements seemed astounding at the time, but it was the eventual explanation for emission spectra by Neils Bohr in 1913 that ultimately convinced scientists to abandon classical physics and spurred the development of modern quantum mechanics.

Key Concepts and Summary

Light and other forms of electromagnetic radiation move through a vacuum with a constant speed, c , of $2.998 \times 10^8 \text{ m s}^{-1}$. This radiation shows wavelike behavior, which can be characterized by a frequency, ν , and a wavelength, λ , such that $c = \lambda\nu$. Light is an example of a travelling wave. Other important wave phenomena include standing waves, periodic oscillations, and vibrations. Standing waves exhibit quantization, since their wavelengths are limited to discrete integer multiples of some characteristic lengths. Electromagnetic radiation that passes through two closely spaced narrow slits having dimensions roughly similar to the wavelength will show an interference pattern that is a result of constructive and destructive interference of the waves. Electromagnetic radiation also demonstrates properties of particles called photons. The energy of a photon is related to the frequency (or alternatively, the wavelength) of the radiation as $E = h\nu$

(or $E = \frac{hc}{\lambda}$), where h is Planck's constant. That light demonstrates both wavelike and particle-like behavior is known as wave-particle duality. All forms of electromagnetic radiation share these properties, although various forms including X-rays, visible light, microwaves, and radio waves interact differently with matter and have very different practical applications. Electromagnetic radiation can be generated by exciting matter to higher energies, such as by heating it. The emitted light can be either continuous (incandescent sources like the sun) or discrete (from specific types of excited atoms). Continuous spectra often have distributions that can be approximated as blackbody radiation at some appropriate temperature. The line spectrum of hydrogen can be obtained by passing the light from an electrified tube of hydrogen gas through a prism. This line spectrum was simple enough that an empirical formula called the Rydberg formula could be derived from the spectrum. Three historically important paradoxes from the late 19th and early 20th centuries that could not be explained within the existing framework of classical mechanics and classical electromagnetism were the blackbody problem, the photoelectric effect, and the discrete spectra of atoms. The resolution of these paradoxes ultimately led to quantum theories that superseded the classical theories.

Key Equations

- $c = \lambda\nu$
- $E = h\nu = \frac{hc}{\lambda}$, where $h = 6.626 \times 10^{-34} \text{ J s}$
- $\frac{1}{\lambda} = R_{\infty} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

Chemistry End of Chapter Exercises

Exercise:

Problem:

The light produced by a red neon sign is due to the emission of light by excited neon atoms. Qualitatively describe the spectrum produced by passing light from a neon lamp through a prism.

Solution:

The spectrum consists of colored lines, at least one of which (probably the brightest) is red.

Exercise:**Problem:**

An FM radio station found at 103.1 on the FM dial broadcasts at a frequency of $1.031 \times 10^8 \text{ s}^{-1}$ (103.1 MHz). What is the wavelength of these radio waves in meters?

Exercise:**Problem:**

FM-95, an FM radio station, broadcasts at a frequency of $9.51 \times 10^7 \text{ s}^{-1}$ (95.1 MHz). What is the wavelength of these radio waves in meters?

Solution:

3.15 m

Exercise:**Problem:**

A bright violet line occurs at 435.8 nm in the emission spectrum of mercury vapor. What amount of energy, in joules, must be released by an electron in a mercury atom to produce a photon of this light?

Exercise:**Problem:**

Light with a wavelength of 614.5 nm looks orange. What is the energy, in joules, per photon of this orange light? What is the energy in eV ($1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$)?

Solution:

$$3.233 \times 10^{-19} \text{ J}; 2.018 \text{ eV}$$

Exercise:**Problem:**

Heated lithium atoms emit photons of light with an energy of $2.961 \times 10^{-19} \text{ J}$. Calculate the frequency and wavelength of one of these photons. What is the total energy in 1 mole of these photons? What is the color of the emitted light?

Exercise:**Problem:**

A photon of light produced by a surgical laser has an energy of $3.027 \times 10^{-19} \text{ J}$. Calculate the frequency and wavelength of the photon. What is the total energy in 1 mole of photons? What is the color of the emitted light?

Solution:

$$\nu = 4.568 \times 10^{14} \text{ s}^{-1}; \lambda = 656.3 \text{ nm}; \text{Energy mol}^{-1} = 1.823 \times 10^5 \text{ J mol}^{-1}; \text{red}$$

Exercise:**Problem:**

When rubidium ions are heated to a high temperature, two lines are observed in its line spectrum at wavelengths (a) $7.9 \times 10^{-7} \text{ m}$ and (b) $4.2 \times 10^{-7} \text{ m}$. What are the frequencies of the two lines? What color do we see when we heat a rubidium compound?

Exercise:**Problem:**

The emission spectrum of cesium contains two lines whose frequencies are (a) $3.45 \times 10^{14} \text{ Hz}$ and (b) $6.53 \times 10^{14} \text{ Hz}$. What are the wavelengths and energies per photon of the two lines? What color are the lines?

Solution:

(a) $\lambda = 8.69 \times 10^{-7} \text{ m}$; $E = 2.29 \times 10^{-19} \text{ J}$; (b) $\lambda = 4.59 \times 10^{-7} \text{ m}$; $E = 4.33 \times 10^{-19} \text{ J}$; The color of (a) is red; (b) is blue.

Exercise:**Problem:**

Photons of infrared radiation are responsible for much of the warmth we feel when holding our hands before a fire. These photons will also warm other objects. How many infrared photons with a wavelength of $1.5 \times 10^{-6} \text{ m}$ must be absorbed by the water to warm a cup of water (175 g) from 25.0 °C to 40 °C?

Exercise:**Problem:**

One of the radiographic devices used in a dentist's office emits an X-ray of wavelength $2.090 \times 10^{-11} \text{ m}$. What is the energy, in joules, and frequency of this X-ray?

Solution:

$$E = 9.502 \times 10^{-15} \text{ J}; \nu = 1.434 \times 10^{19} \text{ s}^{-1}$$

Exercise:**Problem:**

The eyes of certain reptiles pass a single visual signal to the brain when the visual receptors are struck by photons of a wavelength of 850 nm. If a total energy of $3.15 \times 10^{-14} \text{ J}$ is required to trip the signal, what is the minimum number of photons that must strike the receptor?

Exercise:

Problem:

RGB color television and computer displays use cathode ray tubes that produce colors by mixing red, green, and blue light. If we look at the screen with a magnifying glass, we can see individual dots turn on and off as the colors change. Using a spectrum of visible light, determine the approximate wavelength of each of these colors. What is the frequency and energy of a photon of each of these colors?

Solution:

Red: 660 nm; 4.54×10^{14} Hz; 3.01×10^{-19} J. Green: 520 nm; 5.77×10^{14} Hz; 3.82×10^{-19} J. Blue: 440 nm; 6.81×10^{14} Hz; 4.51×10^{-19} J. Somewhat different numbers are also possible.

Exercise:

Problem: Answer the following questions about a Blu-ray laser:

- (a) The laser on a Blu-ray player has a wavelength of 405 nm. In what region of the electromagnetic spectrum is this radiation? What is its frequency?
- (b) A Blu-ray laser has a power of 5 milliwatts ($1 \text{ watt} = 1 \text{ J s}^{-1}$). How many photons of light are produced by the laser in 1 hour?
- (c) The ideal resolution of a player using a laser (such as a Blu-ray player), which determines how close together data can be stored on a compact disk, is determined using the following formula: $\text{Resolution} = 0.60(\lambda/\text{NA})$, where λ is the wavelength of the laser and NA is the numerical aperture. Numerical aperture is a measure of the size of the spot of light on the disk; the larger the NA, the smaller the spot. In a typical Blu-ray system, $\text{NA} = 0.95$. If the 405-nm laser is used in a Blu-ray player, what is the closest that information can be stored on a Blu-ray disk?
- (d) The data density of a Blu-ray disk using a 405-nm laser is $1.5 \times 10^7 \text{ bits mm}^{-2}$. Disks have an outside diameter of 120 mm and a hole

of 15-mm diameter. How many data bits can be contained on the disk? If a Blu-ray disk can hold 9,400,000 pages of text, how many data bits are needed for a typed page? (Hint: Determine the area of the disk that is available to hold data. The area inside a circle is given by $A = \pi r^2$, where the radius r is one-half of the diameter.)

Exercise:

Problem:

What is the threshold frequency for sodium metal if a photon with frequency $6.66 \times 10^{14} \text{ s}^{-1}$ ejects an electron with $7.74 \times 10^{-20} \text{ J}$ kinetic energy? Will the photoelectric effect be observed if sodium is exposed to orange light?

Solution:

$5.49 \times 10^{14} \text{ s}^{-1}$; no

Glossary

amplitude

extent of the displacement caused by a wave (for sinusoidal waves, it is one-half the difference from the peak height to the trough depth, and the intensity is proportional to the square of the amplitude)

blackbody

idealized perfect absorber of all incident electromagnetic radiation; such bodies emit electromagnetic radiation in characteristic continuous spectra called blackbody radiation

continuous spectrum

electromagnetic radiation given off in an unbroken series of wavelengths (e.g., white light from the sun)

electromagnetic radiation

energy transmitted by waves that have an electric-field component and a magnetic-field component

electromagnetic spectrum

range of energies that electromagnetic radiation can comprise, including radio, microwaves, infrared, visible, ultraviolet, X-rays, and gamma rays; since electromagnetic radiation energy is proportional to the frequency and inversely proportional to the wavelength, the spectrum can also be specified by ranges of frequencies or wavelengths

frequency (ν)

number of wave cycles (peaks or troughs) that pass a specified point in space per unit time

hertz (Hz)

the unit of frequency, which is the number of cycles per second, s^{-1}

intensity

property of wave-propagated energy related to the amplitude of the wave, such as brightness of light or loudness of sound

interference pattern

pattern typically consisting of alternating bright and dark fringes; it results from constructive and destructive interference of waves

line spectrum

electromagnetic radiation emitted at discrete wavelengths by a specific atom (or atoms) in an excited state

node

any point of a standing wave with zero amplitude

photon

smallest possible packet of electromagnetic radiation, a particle of light

quantization

occurring only in specific discrete values, not continuous

standing wave

(also, stationary wave) localized wave phenomenon characterized by discrete wavelengths determined by the boundary conditions used to generate the waves; standing waves are inherently quantized

wave

oscillation that can transport energy from one point to another in space

wavelength (λ)

distance between two consecutive peaks or troughs in a wave

wave-particle duality

term used to describe the fact that elementary particles including matter exhibit properties of both particles (including localized position, momentum) and waves (including nonlocalization, wavelength, frequency)

The Bohr Model

By the end of this section, you will be able to:

- Describe the Bohr model of the hydrogen atom
- Use the Rydberg equation to calculate energies of light emitted or absorbed by hydrogen atoms

Following the work of Ernest Rutherford and his colleagues in the early twentieth century, the picture of atoms consisting of tiny dense nuclei surrounded by lighter and even tinier electrons continually moving about the nucleus was well established. This picture was called the planetary model, since it pictured the atom as a miniature “solar system” with the electrons orbiting the nucleus like planets orbiting the sun. The simplest atom is hydrogen, consisting of a single proton as the nucleus about which a single electron moves. The electrostatic force attracting the electron to the proton depends only on the distance between the two particles. The electrostatic force has the same form as the gravitational force between two mass particles except that the electrostatic force depends on the magnitudes of the charges on the particles (+1 for the proton and -1 for the electron) instead of the magnitudes of the particle masses that govern the gravitational force. Since forces can be derived from potentials, it is convenient to work with potentials instead, since they are forms of energy. The electrostatic potential is also called the Coulomb potential. Because the electrostatic potential has the same form as the gravitational potential, according to classical mechanics, the equations of motion should be similar, with the electron moving around the nucleus in circular or elliptical orbits (hence the label “planetary” model of the atom). Potentials of the form $V(r)$ that depend only on the radial distance r are known as central potentials. Central potentials have spherical symmetry, and so rather than specifying the position of the electron in the usual Cartesian coordinates (x, y, z) , it is more convenient to use polar spherical coordinates centered at the nucleus, consisting of a linear coordinate r and two angular coordinates, usually specified by the Greek letters theta (θ) and phi (Φ). These coordinates are similar to the ones used in GPS devices and most smart phones that track positions on our (nearly) spherical earth, with the two angular coordinates specified by the latitude and longitude, and the linear coordinate specified by sea-level elevation. Because of the spherical symmetry of central

potentials, the energy and angular momentum of the classical hydrogen atom are constants, and the orbits are constrained to lie in a plane like the planets orbiting the sun. This classical mechanics description of the atom is incomplete, however, since an electron moving in an elliptical orbit would be accelerating (by changing direction) and, according to classical electromagnetism, it should continuously emit electromagnetic radiation. This loss in orbital energy should result in the electron's orbit getting continually smaller until it spirals into the nucleus, implying that atoms are inherently unstable.

In 1913, Niels Bohr attempted to resolve the atomic paradox by ignoring classical electromagnetism's prediction that the orbiting electron in hydrogen would continuously emit light. Instead, he incorporated into the classical mechanics description of the atom Planck's ideas of quantization and Einstein's finding that light consists of photons whose energy is proportional to their frequency. Bohr assumed that the electron orbiting the nucleus would not normally emit any radiation (the stationary state hypothesis), but it would emit or absorb a photon if it moved to a different orbit. The energy absorbed or emitted would reflect differences in the orbital energies according to this equation:

Equation:

$$|\Delta E| = |E_f - E_i| = h\nu = \frac{hc}{\lambda}$$

In this equation, h is Planck's constant and E_i and E_f are the initial and final orbital energies, respectively. The absolute value of the energy difference is used, since frequencies and wavelengths are always positive. Instead of allowing for continuous values for the angular momentum, energy, and orbit radius, Bohr assumed that only discrete values for these could occur (actually, quantizing any one of these would imply that the other two are also quantized). Bohr's expression for the quantized energies is:

Equation:

$$E_n = -\frac{k}{n^2}, n = 1, 2, 3, \dots$$

In this expression, k is a constant comprising fundamental constants such as the electron mass and charge and Planck's constant. Inserting the expression for the orbit energies into the equation for ΔE gives

Equation:

$$\Delta E = k \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = \frac{hc}{\lambda}$$

or

Equation:

$$\frac{1}{\lambda} = \frac{k}{hc} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

which is identical to the Rydberg equation for $R_\infty = \frac{k}{hc}$. When Bohr calculated his theoretical value for the Rydberg constant, R_∞ , and compared it with the experimentally accepted value, he got excellent agreement. Since the Rydberg constant was one of the most precisely measured constants at that time, this level of agreement was astonishing and meant that **Bohr's model** was taken seriously, despite the many assumptions that Bohr needed to derive it.

The lowest few energy levels are shown in [\[link\]](#). One of the fundamental laws of physics is that matter is most stable with the lowest possible energy. Thus, the electron in a hydrogen atom usually moves in the $n = 1$ orbit, the orbit in which it has the lowest energy. When the electron is in this lowest energy orbit, the atom is said to be in its **ground electronic state** (or simply ground state). If the atom receives energy from an outside source, it is possible for the electron to move to an orbit with a higher n value and the atom is now in an **excited electronic state** (or simply an excited state) with a higher energy. When an electron transitions from an excited state (higher energy orbit) to a less excited state, or ground state, the difference in energy is emitted as a photon. Similarly, if a photon is absorbed by an atom, the energy of the photon moves an electron from a lower energy orbit up to a

more excited one. We can relate the energy of electrons in atoms to what we learned previously about energy. The law of conservation of energy says that we can neither create nor destroy energy. Thus, if a certain amount of external energy is required to excite an electron from one energy level to another, that same amount of energy will be liberated when the electron returns to its initial state ([\[link\]](#)). In effect, an atom can “store” energy by using it to promote an electron to a state with a higher energy and release it when the electron returns to a lower state. The energy can be released as one quantum of energy, as the electron returns to its ground state (say, from $n = 5$ to $n = 1$), or it can be released as two or more smaller quanta as the electron falls to an intermediate state, then to the ground state (say, from $n = 5$ to $n = 4$, emitting one quantum, then to $n = 1$, emitting a second quantum).

Since Bohr’s model involved only a single electron, it could also be applied to the single electron ions He^+ , Li^{2+} , Be^{3+} , and so forth, which differ from hydrogen only in their nuclear charges, and so one-electron atoms and ions are collectively referred to as hydrogen-like atoms. The energy expression for hydrogen-like atoms is a generalization of the hydrogen atom energy, in which Z is the nuclear charge (+1 for hydrogen, +2 for He, +3 for Li, and so on) and k has a value of $2.179 \times 10^{-18} \text{ J}$.

Equation:

$$E_n = -\frac{kZ^2}{n^2}$$

The sizes of the circular orbits for hydrogen-like atoms are given in terms of their radii by the following expression, in which α_0 is a constant called the Bohr radius, with a value of $5.292 \times 10^{-11} \text{ m}$:

Equation:

$$r = \frac{n^2}{Z} \alpha_0$$

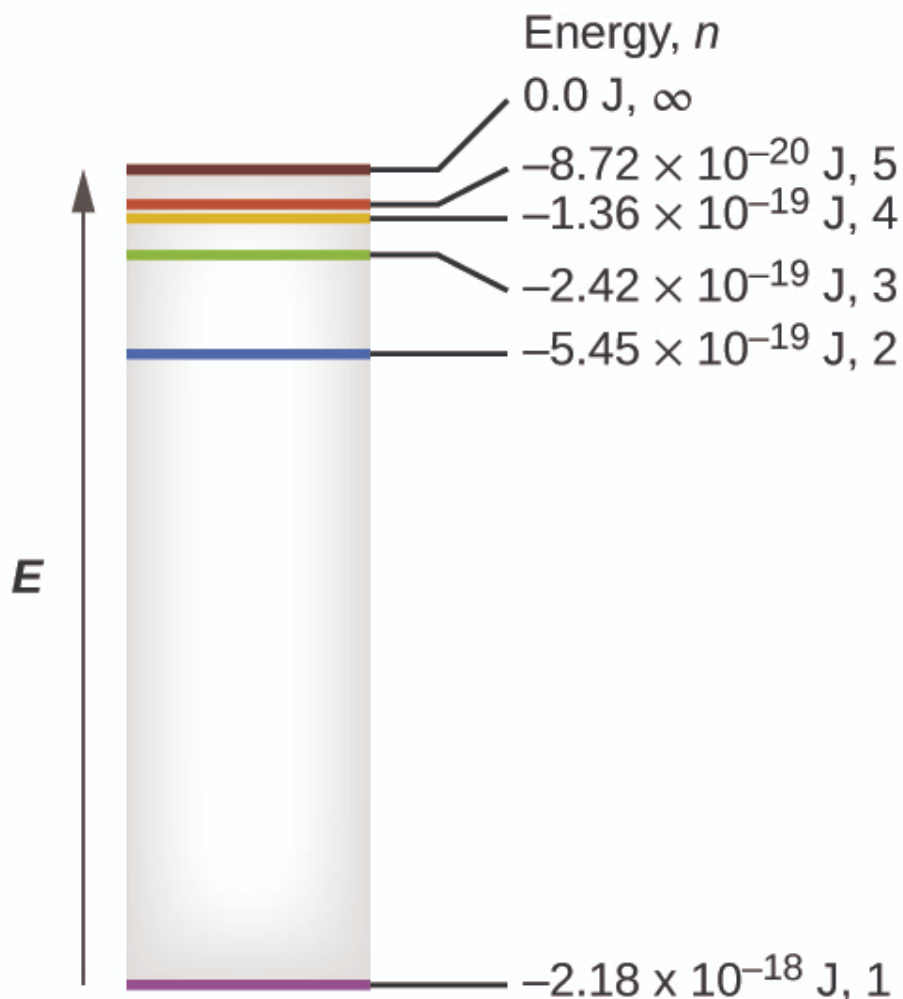
The equation also shows us that as the electron’s energy increases (as n increases), the electron is found at greater distances from the nucleus. This

is implied by the inverse dependence on r in the Coulomb potential, since, as the electron moves away from the nucleus, the electrostatic attraction between it and the nucleus decreases, and it is held less tightly in the atom. Note that as n gets larger and the orbits get larger, their energies get closer to zero, and so the limits $n \rightarrow \infty$, $r \rightarrow \infty$, and $E \rightarrow 0$ imply that $E = 0$ corresponds to the ionization limit where the electron is completely removed from the nucleus. Thus, for hydrogen in the ground state $n = 1$, the ionization energy would be:

Equation:

$$\Delta E = E_{n \rightarrow \infty} - E_1 = 0 - (-13.6 \text{ eV}) = 13.6 \text{ eV}$$

With three extremely puzzling paradoxes now solved (blackbody radiation, the photoelectric effect, and the hydrogen atom), and all involving Planck's constant in a fundamental manner, it became clear to most physicists at that time that the classical theories that worked so well in the macroscopic world were fundamentally flawed and could not be extended down into the microscopic domain of atoms and molecules. Unfortunately, despite Bohr's remarkable achievement in deriving a theoretical expression for the Rydberg constant, he was unable to extend his theory to the next simplest atom, He, which only has two electrons. Bohr's model was severely flawed, since it was still based on the classical mechanics notion of precise orbits, a concept that was later found to be untenable in the microscopic domain, when a proper model of quantum mechanics was developed to supersede classical mechanics.



Quantum numbers and energy levels in a hydrogen atom. The more negative the calculated value, the lower the energy.

Example:

Calculating the Energy of an Electron in a Bohr Orbit

Early researchers were very excited when they were able to predict the energy of an electron at a particular distance from the nucleus in a hydrogen atom. If a spark promotes the electron in a hydrogen atom into an orbit with $n = 3$, what is the calculated energy, in joules, of the electron?

Solution

The energy of the electron is given by this equation:

Equation:

$$E = \frac{-kZ^2}{n^2}$$

The atomic number, Z , of hydrogen is 1; $k = 2.179 \times 10^{-18} \text{ J}$; and the electron is characterized by an n value of 3. Thus,

Equation:

$$E = \frac{-(2.179 \times 10^{-18} \text{ J}) \times (1)^2}{(3)^2} = -2.421 \times 10^{-19} \text{ J}$$

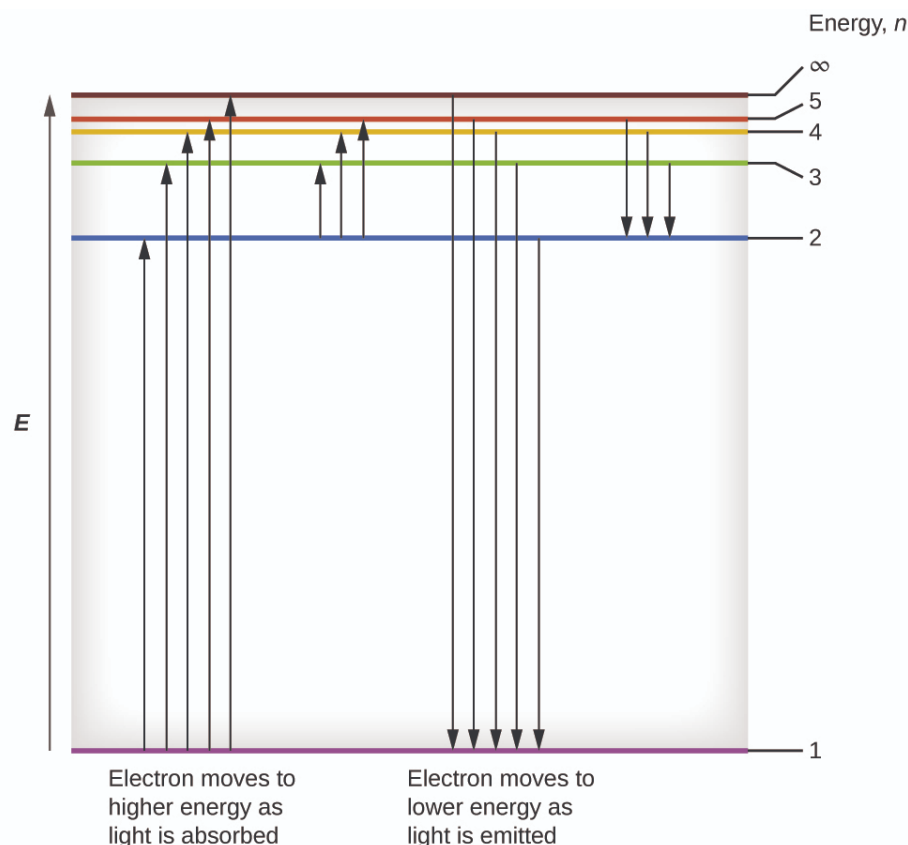
Check Your Learning

The electron in [\[link\]](#) is promoted even further to an orbit with $n = 6$. What is its new energy?

Note:

Answer:

$$-6.053 \times 10^{-20} \text{ J}$$



The horizontal lines show the relative energy of orbits in the Bohr model of the hydrogen atom, and the vertical arrows depict the energy of photons absorbed (left) or emitted (right) as electrons move between these orbits.

Example:

Calculating the Energy and Wavelength of Electron Transitions in a One-electron (Bohr) System

What is the energy (in joules) and the wavelength (in meters) of the line in the spectrum of hydrogen that represents the movement of an electron from Bohr orbit with $n = 4$ to the orbit with $n = 6$? In what part of the electromagnetic spectrum do we find this radiation?

Solution

In this case, the electron starts out with $n = 4$, so $n_1 = 4$. It comes to rest in the $n = 6$ orbit, so $n_2 = 6$. The difference in energy between the two states is given by this expression:

Equation:

$$\Delta E = E_1 - E_2 = 2.179 \times 10^{-18} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Equation:

$$\Delta E = 2.179 \times 10^{-18} \left(\frac{1}{4^2} - \frac{1}{6^2} \right) \text{ J}$$

Equation:

$$\Delta E = 2.179 \times 10^{-18} \left(\frac{1}{16} - \frac{1}{36} \right) \text{ J}$$

Equation:

$$\Delta E = 7.566 \times 10^{-20} \text{ J}$$

This energy difference is positive, indicating a photon enters the system (is absorbed) to excite the electron from the $n = 4$ orbit up to the $n = 6$ orbit. The wavelength of a photon with this energy is found by the expression $E = \frac{hc}{\lambda}$. Rearrangement gives:

Equation:

$$\lambda = \frac{hc}{E}$$

Equation:

$$\begin{aligned} &= (6.626 \times 10^{-34} \text{ J} \cdot \text{s}) \times \frac{2.998 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{7.566 \times 10^{-20} \text{ J}} \\ &= 2.626 \times 10^{-6} \text{ m} \end{aligned}$$

From [\[link\]](#), we can see that this wavelength is found in the infrared portion of the electromagnetic spectrum.

Check Your Learning

What is the energy in joules and the wavelength in meters of the photon produced when an electron falls from the $n = 5$ to the $n = 3$ level in a He^+ ion ($Z = 2$ for He^+)?

Note:

Answer:

$6.198 \times 10^{-19} \text{ J}$; $3.205 \times 10^{-7} \text{ m}$

Bohr's model of the hydrogen atom provides insight into the behavior of matter at the microscopic level, but it does not account for electron–electron interactions in atoms with more than one electron. It does introduce several important features of all models used to describe the distribution of electrons in an atom. These features include the following:

- The energies of electrons (energy levels) in an atom are quantized, described by **quantum numbers**: integer numbers having only specific allowed value and used to characterize the arrangement of electrons in an atom.
- An electron's energy increases with increasing distance from the nucleus.
- The discrete energies (lines) in the spectra of the elements result from quantized electronic energies.

Of these features, the most important is the postulate of quantized energy levels for an electron in an atom. As a consequence, the model laid the foundation for the quantum mechanical model of the atom. Bohr won a Nobel Prize in Physics for his contributions to our understanding of the structure of atoms and how that is related to line spectra emissions.

Key Concepts and Summary

Bohr incorporated Planck's and Einstein's quantization ideas into a model of the hydrogen atom that resolved the paradox of atom stability and discrete spectra. The Bohr model of the hydrogen atom explains the connection between the quantization of photons and the quantized emission from atoms. Bohr described the hydrogen atom in terms of an electron moving in a circular orbit about a nucleus. He postulated that the electron was restricted to certain orbits characterized by discrete energies. Transitions between these allowed orbits result in the absorption or emission of photons. When an electron moves from a higher-energy orbit to a more stable one, energy is emitted in the form of a photon. To move an electron from a stable orbit to a more excited one, a photon of energy must be absorbed. Using the Bohr model, we can calculate the energy of an electron and the radius of its orbit in any one-electron system.

Key Equations

- $E_n = -\frac{kZ^2}{n^2}, n = 1, 2, 3, \dots$
- $\Delta E = kZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$
- $r = \frac{n^2}{Z} a_0$

Chemistry End of Chapter Exercises

Exercise:

Problem:

Why is the electron in a Bohr hydrogen atom bound less tightly when it has a quantum number of 3 than when it has a quantum number of 1?

Exercise:

Problem:

What does it mean to say that the energy of the electrons in an atom is quantized?

Solution:

Quantized energy means that the electrons can possess only certain discrete energy values; values between those quantized values are not permitted.

Exercise:**Problem:**

Using the Bohr model, determine the energy, in joules, necessary to ionize a ground-state hydrogen atom. Show your calculations.

Exercise:**Problem:**

The electron volt (eV) is a convenient unit of energy for expressing atomic-scale energies. It is the amount of energy that an electron gains when subjected to a potential of 1 volt; $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$. Using the Bohr model, determine the energy, in electron volts, of the photon produced when an electron in a hydrogen atom moves from the orbit with $n = 5$ to the orbit with $n = 2$. Show your calculations.

Solution:

$$\begin{aligned} E &= E_2 - E_5 = 2.179 \times 10^{-18} \left(\frac{1}{n_2^2} - \frac{1}{n_5^2} \right) \text{ J} \\ &= 2.179 \times 10^{-18} \left(\frac{1}{2^2} - \frac{1}{5^2} \right) = 4.576 \times 10^{-19} \text{ J} \\ &= \frac{4.576 \times 10^{-19} \cancel{\text{J}}}{1.602 \times 10^{-19} \cancel{\text{J}} \text{ eV}^{-1}} = 2.856 \text{ eV} \end{aligned}$$

Exercise:**Problem:**

Using the Bohr model, determine the lowest possible energy, in joules, for the electron in the Li^{2+} ion.

Exercise:

Problem:

Using the Bohr model, determine the lowest possible energy for the electron in the He^+ ion.

Solution:

$$-8.716 \times 10^{-18} \text{ J}$$

Exercise:**Problem:**

Using the Bohr model, determine the energy of an electron with $n = 6$ in a hydrogen atom.

Exercise:**Problem:**

Using the Bohr model, determine the energy of an electron with $n = 8$ in a hydrogen atom.

Solution:

$$-3.405 \times 10^{-20} \text{ J}$$

Exercise:**Problem:**

How far from the nucleus in angstroms ($1 \text{ angstrom} = 1 \times 10^{-10} \text{ m}$) is the electron in a hydrogen atom if it has an energy of $-8.72 \times 10^{-20} \text{ J}$?

Exercise:**Problem:**

What is the radius, in angstroms, of the orbital of an electron with $n = 8$ in a hydrogen atom?

Solution:

33.9 Å

Exercise:**Problem:**

Using the Bohr model, determine the energy in joules of the photon produced when an electron in a He^+ ion moves from the orbit with $n = 5$ to the orbit with $n = 2$.

Exercise:**Problem:**

Using the Bohr model, determine the energy in joules of the photon produced when an electron in a Li^{2+} ion moves from the orbit with $n = 2$ to the orbit with $n = 1$.

Solution:

$1.471 \times 10^{-17} \text{ J}$

Exercise:**Problem:**

Consider a large number of hydrogen atoms with electrons randomly distributed in the $n = 1, 2, 3$, and 4 orbits.

- (a) How many different wavelengths of light are emitted by these atoms as the electrons fall into lower-energy orbitals?
- (b) Calculate the lowest and highest energies of light produced by the transitions described in part (a).
- (c) Calculate the frequencies and wavelengths of the light produced by the transitions described in part (b).

Exercise:

Problem:

How are the Bohr model and the Rutherford model of the atom similar? How are they different?

Solution:

Both involve a relatively heavy nucleus with electrons moving around it, although strictly speaking, the Bohr model works only for one-electron atoms or ions. According to classical mechanics, the Rutherford model predicts a miniature “solar system” with electrons moving about the nucleus in circular or elliptical orbits that are confined to planes. If the requirements of classical electromagnetic theory that electrons in such orbits would emit electromagnetic radiation are ignored, such atoms would be stable, having constant energy and angular momentum, but would not emit any visible light (contrary to observation). If classical electromagnetic theory is applied, then the Rutherford atom would emit electromagnetic radiation of continually increasing frequency (contrary to the observed discrete spectra), thereby losing energy until the atom collapsed in an absurdly short time (contrary to the observed long-term stability of atoms). The Bohr model retains the classical mechanics view of circular orbits confined to planes having constant energy and angular momentum, but restricts these to quantized values dependent on a single quantum number, n . The orbiting electron in Bohr’s model is assumed not to emit any electromagnetic radiation while moving about the nucleus in its stationary orbits, but the atom can emit or absorb electromagnetic radiation when the electron changes from one orbit to another. Because of the quantized orbits, such “quantum jumps” will produce discrete spectra, in agreement with observations.

Exercise:

Problem:

The spectra of hydrogen and of calcium are shown in [\[link\]](#). What causes the lines in these spectra? Why are the colors of the lines different? Suggest a reason for the observation that the spectrum of calcium is more complicated than the spectrum of hydrogen.

Glossary

Bohr's model of the hydrogen atom

structural model in which an electron moves around the nucleus only in circular orbits, each with a specific allowed radius; the orbiting electron does not normally emit electromagnetic radiation, but does so when changing from one orbit to another.

excited state

state having an energy greater than the ground-state energy

ground state

state in which the electrons in an atom, ion, or molecule have the lowest energy possible

quantum number

integer number having only specific allowed values and used to characterize the arrangement of electrons in an atom

Periodic Variations in Element Properties

By the end of this section, you will be able to:

- Describe and explain the observed trends in atomic size, ionization energy, and electron affinity of the elements

The elements in groups (vertical columns) of the periodic table exhibit similar chemical behavior. This similarity occurs because the members of a group have the same number and distribution of electrons in their valence shells. However, there are also other patterns in chemical properties on the periodic table. For example, as we move down a group, the metallic character of the atoms increases. Oxygen, at the top of group 16 (6A), is a colorless gas; in the middle of the group, selenium is a semiconducting solid; and, toward the bottom, polonium is a silver-grey solid that conducts electricity.

As we go across a period from left to right, we add a proton to the nucleus and an electron to the valence shell with each successive element. As we go down the elements in a group, the number of electrons in the valence shell remains constant, but the principal quantum number increases by one each time. An understanding of the electronic structure of the elements allows us to examine some of the properties that govern their chemical behavior. These properties vary periodically as the electronic structure of the elements changes. They are (1) size (radius) of atoms and ions, (2) ionization energies, and (3) electron affinities.

Note:

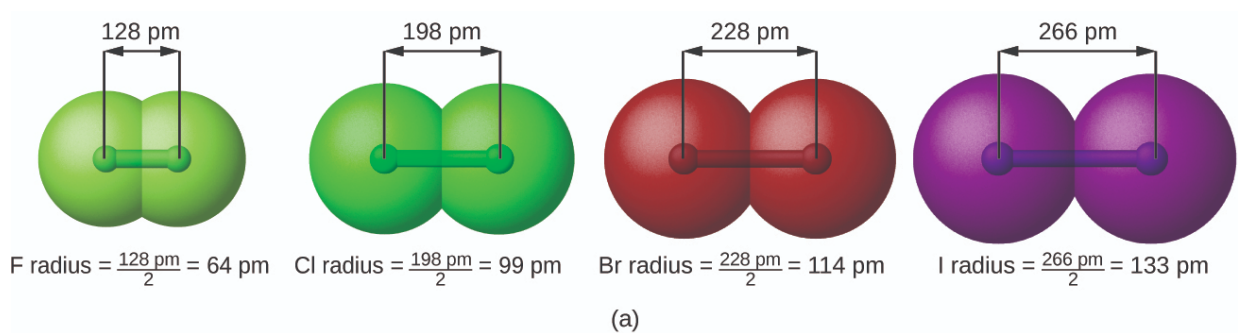


Explore [visualizations](#) of the periodic trends discussed in this section (and many more trends). With just a few clicks, you can create three-dimensional versions of the periodic table showing atomic size or graphs of ionization energies from all measured elements.

Variation in Covalent Radius

The quantum mechanical picture makes it difficult to establish a definite size of an atom. However, there are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the **covalent radius** ([link](#)), which is defined as one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond (this measurement is possible because atoms within molecules still retain much of their atomic identity). We know that as we scan down a group, the principal quantum number, n , increases by one for each element. Thus, the electrons are being added to a region of space that is increasingly distant from the nucleus. Consequently, the size of the atom (and its covalent radius) must increase as we increase the distance of the outermost electrons from the nucleus. This trend is illustrated for the covalent radii of the halogens in [link](#) and [link](#). The trends for the entire periodic table can be seen in [link](#).

Covalent Radii of the Halogen Group Elements		
Atom	Covalent radius (pm)	Nuclear charge
F	64	+9
Cl	99	+17
Br	114	+35
I	133	+53
At	148	+85



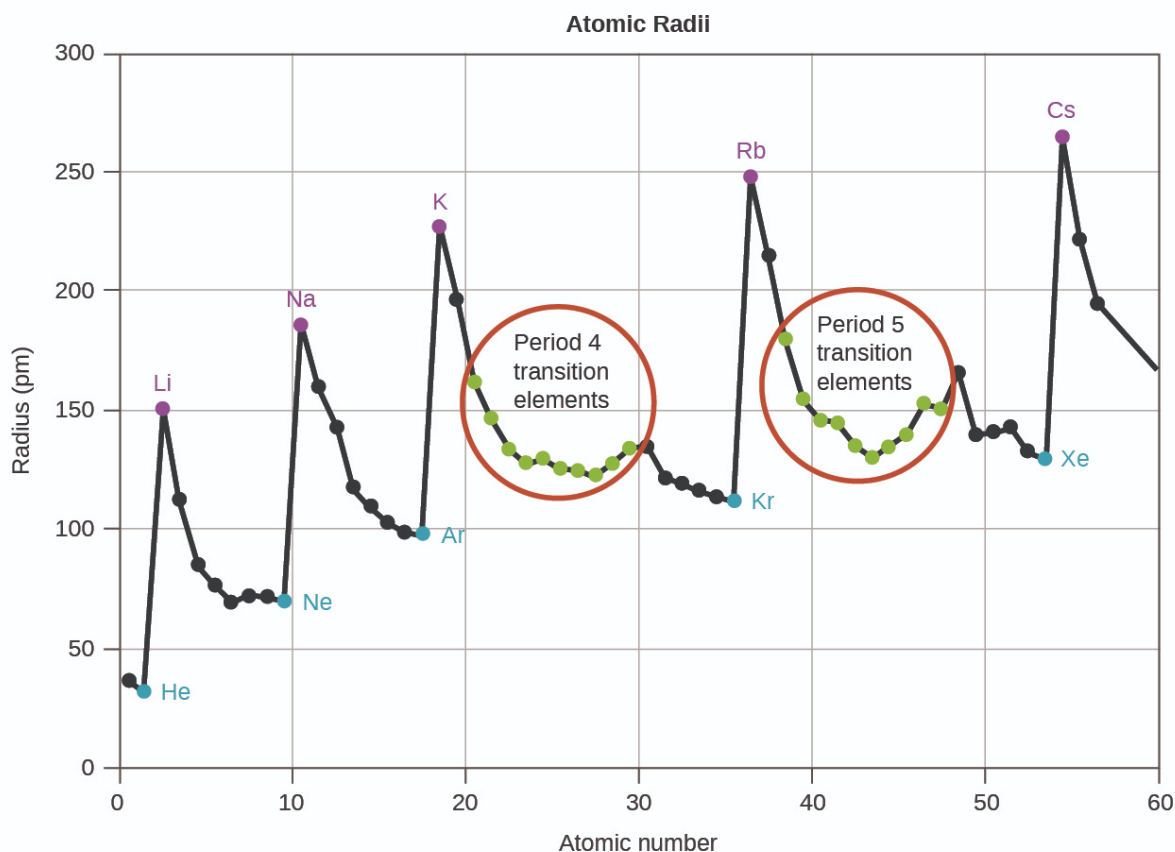
Periodic Table of the Elements

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

(b)

(a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens

increases down the group as n increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period.



Within each period, the trend in atomic radius decreases as Z increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as Z increases.

As shown in [\[link\]](#), as we move across a period from left to right, we generally find that each element has a smaller covalent radius than the element preceding it. This might seem counterintuitive because it implies that atoms with more electrons have a smaller atomic radius. This can be explained with the concept of **effective nuclear charge, Z_{eff}** . This is the pull exerted on a specific electron by the nucleus, taking into account any electron–electron repulsions. For hydrogen, there is only one electron and so the nuclear charge (Z) and the effective nuclear charge (Z_{eff}) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

Equation:

$$Z_{\text{eff}} = Z - \text{shielding}$$

Shielding is determined by the probability of another electron being between the electron of interest and the nucleus, as well as by the electron–electron repulsions the electron of interest encounters. Core electrons are adept at shielding, while electrons in the same valence shell do not block the nuclear attraction experienced by each other as efficiently. Thus, each time we move from one element to the next across a period, Z increases by one, but the shielding increases only slightly. Thus, Z_{eff} increases as we move from left to right across a period. The stronger pull (higher effective nuclear charge) experienced by electrons on the right side of the periodic table draws them closer to the nucleus, making the covalent radii smaller.

Thus, as we would expect, the outermost or valence electrons are easiest to remove because they have the highest energies, are shielded more, and are farthest from the nucleus. As a general rule, when the representative elements form cations, they do so by the loss of the ns or np electrons that were added last in the Aufbau process. The transition elements, on the other hand, lose the ns electrons before they begin to lose the $(n - 1)d$ electrons, even though the ns electrons are added first, according to the Aufbau principle.

Example:**Sorting Atomic Radii**

Predict the order of increasing covalent radius for Ge, Fl, Br, Kr.

Solution

Radius increases as we move down a group, so $\text{Ge} < \text{Fl}$ (Note: Fl is the symbol for flerovium, element 114, NOT fluorine). Radius decreases as we move across a period, so $\text{Kr} < \text{Br} < \text{Ge}$. Putting the trends together, we obtain $\text{Kr} < \text{Br} < \text{Ge} < \text{Fl}$.

Check Your Learning

Give an example of an atom whose size is smaller than fluorine.

Note:**Answer:**

Ne or He

Variation in Ionic Radii

Ionic radius is the measure used to describe the size of an ion. A cation always has fewer electrons and the same number of protons as the parent atom; it is smaller than the atom from which it is derived ([\[link\]](#)). For example, the covalent radius of an aluminum atom ($1s^2 2s^2 2p^6 3s^2 3p^1$) is 118 pm, whereas the ionic radius of an Al^{3+} ($1s^2 2s^2 2p^6$) is 68 pm. As electrons are removed from the outer valence shell, the remaining core electrons occupying smaller shells experience a greater effective nuclear charge Z_{eff} (as discussed) and are drawn even closer to the nucleus.

 Al 118	 S 104
 Al ³⁺ 68	 S ²⁻ 170

The radius for a cation is smaller than the parent atom (Al), due to the lost electrons; the radius for an anion is larger than the parent (S), due to the gained electrons.

Cations with larger charges are smaller than cations with smaller charges (e.g., V²⁺ has an ionic radius of 79 pm, while that of V³⁺ is 64 pm). Proceeding down the groups of the periodic table, we find that cations of successive elements with the same charge generally have larger radii, corresponding to an increase in the principal quantum number, n .

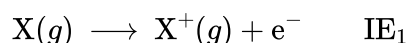
An anion (negative ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in Z_{eff} per electron. Both effects (the increased number of electrons and the decreased Z_{eff}) cause the radius of an anion to be larger than that of the parent atom ([\[link\]](#)). For example, a sulfur atom ([Ne]3s²3p⁴) has a covalent radius of 104 pm, whereas the ionic radius of the sulfide anion ([Ne]3s²3p⁶) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

Atoms and ions that have the same electron configuration are said to be **isoelectronic**. Examples of isoelectronic species are N³⁻, O²⁻, F⁻, Ne, Na⁺, Mg²⁺, and Al³⁺ (1s²2s²2p⁶). Another isoelectronic series is P³⁻, S²⁻, Cl⁻, Ar, K⁺, Ca²⁺, and Sc³⁺ ([Ne]3s²3p⁶). For atoms or ions that are isoelectronic, the number of protons determines the size. The greater the nuclear charge, the smaller the radius in a series of isoelectronic ions and atoms.

Variation in Ionization Energies

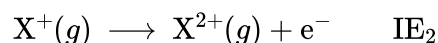
The amount of energy required to remove the most loosely bound electron from a gaseous atom in its ground state is called its first **ionization energy** (IE₁). The first ionization energy for an element, X, is the energy required to form a cation with +1 charge:

Equation:



The energy required to remove the second most loosely bound electron is called the second ionization energy (IE₂).

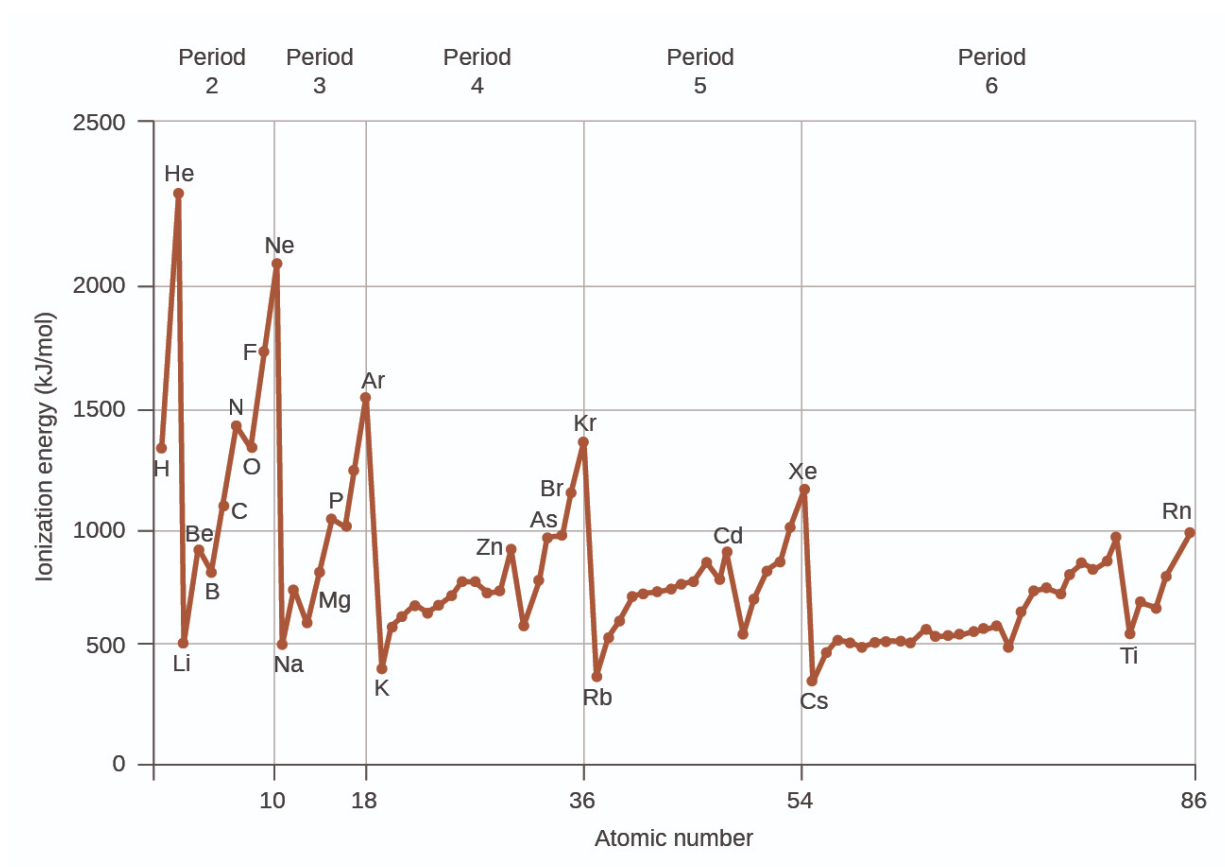
Equation:



The energy required to remove the third electron is the third ionization energy, and so on. Energy is always required to remove electrons from atoms or ions, so ionization processes are endothermic and IE values are always positive. For larger atoms, the most loosely bound electron is located farther

from the nucleus and so is easier to remove. Thus, as size (atomic radius) increases, the ionization energy should decrease. Relating this logic to what we have just learned about radii, we would expect first ionization energies to decrease down a group and to increase across a period.

[\[link\]](#) graphs the relationship between the first ionization energy and the atomic number of several elements. The values of first ionization energy for the elements are given in [\[link\]](#). Within a period, the IE_1 generally increases with increasing Z . Down a group, the IE_1 value generally decreases with increasing Z . There are some systematic deviations from this trend, however. Note that the ionization energy of boron (atomic number 5) is less than that of beryllium (atomic number 4) even though the nuclear charge of boron is greater by one proton. This can be explained because the energy of the subshells increases as l increases, due to penetration and shielding (as discussed previously in this chapter). Within any one shell, the s electrons are lower in energy than the p electrons. This means that an s electron is harder to remove from an atom than a p electron in the same shell. The electron removed during the ionization of beryllium ($[\text{He}]2s^2$) is an s electron, whereas the electron removed during the ionization of boron ($[\text{He}]2s^22p^1$) is a p electron; this results in a lower first ionization energy for boron, even though its nuclear charge is greater by one proton. Thus, we see a small deviation from the predicted trend occurring each time a new subshell begins.

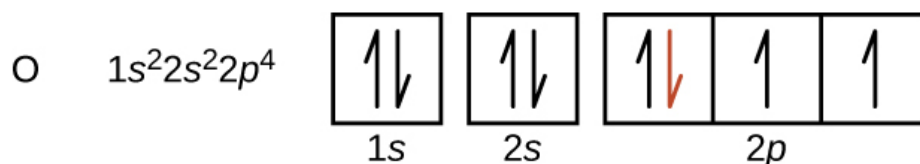


The first ionization energy of the elements in the first five periods are plotted against their atomic number.

Period		First Ionization Energies of Some Elements (kJ/mol)																Group	
		1	2											13	14	15	16	17	18
1		H 1310																	He 2370
2		Li 520	Be 900											B 800	C 1090	N 1400	O 1310	F 1680	Ne 2080
3		Na 490	Mg 730											Al 580	Si 780	P 1060	S 1000	Cl 1250	Ar 1520
4		K 420	Ca 590	Sc 630	Ti 660	V 650	Cr 660	Mn 710	Fe 760	Co 760	Ni 730	Cu 740	Zn 910	Ga 580	Ge 780	As 960	Se 950	Br 1140	Kr 1350
5		Rb 400	Sr 550	Y 620	Zr 660	Nb 670	Mo 680	Tc 700	Ru 710	Rh 720	Pd 800	Ag 730	Cd 870	In 560	Sn 700	Sb 830	Te 870	I 1010	Xe 1170
6		Cs 380	Ba 500	La 540	Hf 700	Ta 760	W 770	Re 760	Os 840	Ir 890	Pt 870	Au 890	Hg 1000	Tl 590	Pb 710	Bi 800	Po 810	At ...	Rn 1030
7		Fr ...	Ra 510																

This version of the periodic table shows the first ionization energy (IE_1), in kJ/mol, of selected elements.

Another deviation occurs as orbitals become more than one-half filled. The first ionization energy for oxygen is slightly less than that for nitrogen, despite the trend in increasing IE_1 values across a period. Looking at the orbital diagram of oxygen, we can see that removing one electron will eliminate the electron–electron repulsion caused by pairing the electrons in the $2p$ orbital and will result in a half-filled orbital (which is energetically favorable). Analogous changes occur in succeeding periods (note the dip for sulfur after phosphorus in [\[link\]](#)).



Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation. Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge. Thus, successive ionization energies for one element always increase. As seen in [\[link\]](#), there is a large increase in the ionization energies for each element. This jump corresponds to removal of the core electrons, which are harder to remove than the valence electrons. For example, Sc and Ga both have three valence electrons, so the rapid increase in ionization energy occurs after the third ionization.

Successive Ionization Energies for Selected Elements (kJ/mol)							
Element	IE ₁	IE ₂	IE ₃	IE ₄	IE ₅	IE ₆	IE ₇
K	418.8	3051.8	4419.6	5876.9	7975.5	9590.6	11343
Ca	589.8	1145.4	4912.4	6490.6	8153.0	10495.7	12272.9
Sc	633.1	1235.0	2388.7	7090.6	8842.9	10679.0	13315.0
Ga	578.8	1979.4	2964.6	6180	8298.7	10873.9	13594.8
Ge	762.2	1537.5	3302.1	4410.6	9021.4	Not available	Not available
As	944.5	1793.6	2735.5	4836.8	6042.9	12311.5	Not available

Example:

Ranking Ionization Energies

Predict the order of increasing energy for the following processes: IE₁ for Al, IE₁ for Tl, IE₂ for Na, IE₃ for Al.

Solution

Removing the 6p¹ electron from Tl is easier than removing the 3p¹ electron from Al because the higher *n* orbital is farther from the nucleus, so IE₁(Tl) < IE₁(Al). Ionizing the third electron from Al (Al²⁺ → Al³⁺ + e[−]) requires more energy because the cation Al²⁺ exerts a stronger pull on the electron than the neutral Al atom, so IE₁(Al) < IE₃(Al). The second ionization energy for sodium removes a core electron, which is a much higher energy process than removing valence electrons. Putting this all together, we obtain: IE₁(Tl) < IE₁(Al) < IE₃(Al) < IE₂(Na).

Check Your Learning

Which has the lowest value for IE₁: O, Po, Pb, or Ba?

Note:

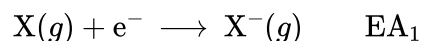
Answer:

Ba

Variation in Electron Affinities

The **electron affinity** [EA] is the energy change for the process of adding an electron to a gaseous atom to form an anion (negative ion).

Equation:



This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in [\[link\]](#). You can see that many of these elements have negative values of EA, which means that energy is released when the gaseous atom accepts an electron. However, for some elements, energy is required for the atom to become negatively charged and the value of their EA is positive. Just as with ionization energy, subsequent EA values are associated with forming ions with more charge. The second EA is the energy associated with adding an electron to an anion to form a -2 ion, and so on.

As we might predict, it becomes easier to add an electron across a series of atoms as the effective nuclear charge of the atoms increases. We find, as we go from left to right across a period, EAs tend to become more negative. The exceptions found among the elements of group 2 (2A), group 15 (5A), and group 18 (8A) can be understood based on the electronic structure of these groups. The noble gases, group 18 (8A), have a completely filled shell and the incoming electron must be added to a higher n level, which is more difficult to do. Group 2 (2A) has a filled ns subshell, and so the next electron added goes into the higher energy np , so, again, the observed EA value is not as the trend would predict. Finally, group 15 (5A) has a half-filled np subshell and the next electron must be paired with an existing np electron. In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

We also might expect the atom at the top of each group to have the largest EA; their first ionization potentials suggest that these atoms have the largest effective nuclear charges. However, as we move down a group, we see that the second element in the group most often has the greatest EA. The reduction of the EA of the first member can be attributed to the small size of the $n = 2$ shell and the resulting large electron–electron repulsions. For example, chlorine, with an EA value of -348 kJ/mol, has the highest value of any element in the periodic table. The EA of fluorine is -322 kJ/mol. When we add an electron to a fluorine atom to form a fluoride anion (F^{-}), we add an electron to the $n = 2$ shell. The electron is attracted to the nucleus, but there is also significant repulsion from the other electrons already present in this small valence shell. The chlorine atom has the same electron configuration in the valence shell, but because the entering electron is going into the $n = 3$ shell, it occupies a considerably larger region of space and the electron–electron repulsions are reduced. The entering electron does not experience as much repulsion and the chlorine atom accepts an additional electron more readily.

Period		Electron Affinity Values for Selected Elements (kJ/mol)																Group	
		1	2											13	14	15	16	17	18
1		H -72																	He +20*
2		Li -60	Be +240*											B -23	C -123	N 0	O -141	F -322	Ne -30
3		Na -53	Mg +230*											Al -44	Si -120	P -74	S -20	Cl -348	Ar +35*
4		K -48	Ca +150*	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga -40*	Ge -115	As -7	Se -195	Br -324	Kr +40*
5		Rb -46	Sr +160*	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In -40*	Sn -121	Sb -101	Te -190	I -295	Xe +40*
6		Cs -45	Ba +50*	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl -50	Pb -101	Bi -101	Po -170	At -270*	Rn +40*
7		Fr	Ra																

* Calculated value

This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.

The properties discussed in this section (size of atoms and ions, effective nuclear charge, ionization energies, and electron affinities) are central to understanding chemical reactivity. For example, because fluorine has an energetically favorable EA and a large energy barrier to ionization (IE), it is much easier to form fluorine anions than cations. Metallic properties including conductivity and malleability (the ability to be formed into sheets) depend on having electrons that can be removed easily. Thus, metallic character increases as we move down a group and decreases across a period in the same trend observed for atomic size because it is easier to remove an electron that is farther away from the nucleus.

Key Concepts and Summary

Electron configurations allow us to understand many periodic trends. Covalent radius increases as we move down a group because the n level (orbital size) increases. Covalent radius mostly decreases as we move left to right across a period because the effective nuclear charge experienced by the electrons increases, and the electrons are pulled in tighter to the nucleus. Anionic radii are larger than the parent atom, while cationic radii are smaller, because the number of valence electrons has changed while the nuclear charge has remained constant. Ionization energy (the energy associated with forming a cation) decreases down a group and mostly increases across a period because it is easier to remove an electron from a larger, higher energy orbital. Electron affinity (the energy associated with forming an anion) is more favorable (exothermic) when electrons are placed into lower energy orbitals, closer to the nucleus. Therefore, electron affinity becomes increasingly negative as we move left to right across the periodic table and decreases as we move down a group. For both IE and electron affinity data, there are exceptions to the trends when dealing with completely filled or half-filled subshells.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Based on their positions in the periodic table, predict which has the smallest atomic radius: Mg, Sr, Si, Cl, I.

Solution:

Cl

Exercise:

Problem:

Based on their positions in the periodic table, predict which has the largest atomic radius: Li, Rb, N, F, I.

Exercise:

Problem:

Based on their positions in the periodic table, predict which has the largest first ionization energy: Mg, Ba, B, O, Te.

Solution:

O

Exercise:

Problem:

Based on their positions in the periodic table, predict which has the smallest first ionization energy: Li, Cs, N, F, I.

Exercise:

Problem:

Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: F, Li, N, Rb

Solution:

Rb < Li < N < F

Exercise:

Problem:

Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: Mg, O, S, Si

Exercise:

Problem:

Atoms of which group in the periodic table have a valence shell electron configuration of ns^2np^3 ?

Solution:

15 (5A)

Exercise:**Problem:**

Atoms of which group in the periodic table have a valence shell electron configuration of ns^2 ?

Exercise:**Problem:**

Based on their positions in the periodic table, list the following atoms in order of increasing radius: Mg, Ca, Rb, Cs.

Solution:

$\text{Mg} < \text{Ca} < \text{Rb} < \text{Cs}$

Exercise:**Problem:**

Based on their positions in the periodic table, list the following atoms in order of increasing radius: Sr, Ca, Si, Cl.

Exercise:**Problem:**

Based on their positions in the periodic table, list the following ions in order of increasing radius: K^+ , Ca^{2+} , Al^{3+} , Si^{4+} .

Solution:

$\text{Si}^{4+} < \text{Al}^{3+} < \text{Ca}^{2+} < \text{K}^+$

Exercise:

Problem: List the following ions in order of increasing radius: Li^+ , Mg^{2+} , Br^- , Te^{2-} .

Exercise:

Problem: Which atom and/or ion is (are) isoelectronic with Br^+ : Se^{2+} , Se, As^- , Kr, Ga^{3+} , Cl^- ?

Solution:

Se, As^-

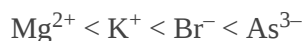
Exercise:

Problem:

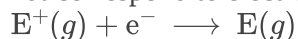
Which of the following atoms and ions is (are) isoelectronic with S^{2+} : Si^{4+} , Cl^{3+} , Ar, As^{3+} , Si, Al^{3+} ?

Exercise:**Problem:**

Compare both the numbers of protons and electrons present in each to rank the following ions in order of increasing radius: As^{3-} , Br^{-} , K^{+} , Mg^{2+} .

Solution:**Exercise:****Problem:**

Of the five elements Al, Cl, I, Na, Rb, which has the most exothermic reaction? (E represents an atom.) What name is given to the energy for the reaction? Hint: note the process depicted does *not* correspond to electron affinity

**Exercise:****Problem:**

Of the five elements Sn, Si, Sb, O, Te, which has the most endothermic reaction? (E represents an atom.) What name is given to the energy for the reaction?

**Solution:**

O, IE_1

Exercise:**Problem:**

The ionic radii of the ions S^{2-} , Cl^{-} , and K^{+} are 184, 181, 138 pm respectively. Explain why these ions have different sizes even though they contain the same number of electrons.

Exercise:**Problem:**

Which main group atom would be expected to have the lowest second ionization energy?

Solution:

Ra

Exercise:

Problem: Explain why Al is a member of group 13 rather than group 3?

Glossary

covalent radius

one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond

effective nuclear charge

charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding

electron affinity

energy required to add an electron to a gaseous atom to form an anion

ionization energy

energy required to remove an electron from a gaseous atom or ion. The associated number (e.g., second ionization energy) corresponds to the charge of the ion produced (X^{2+})

isoelectronic

group of ions or atoms that have identical electron configurations

Introduction

class="introduction"

- Writing and Balancing Chemical Equations
- Classifying Chemical Reactions
- Reaction Stoichiometry
- Reaction Yields
- Quantitative Chemical Analysis

Many
modern
rocket fuels
are solid
mixtures of
substances
combined in
carefully
measured
amounts and
ignited to
yield a
thrust-
generating
chemical
reaction.
(credit:
modificatio
n of work
by NASA)



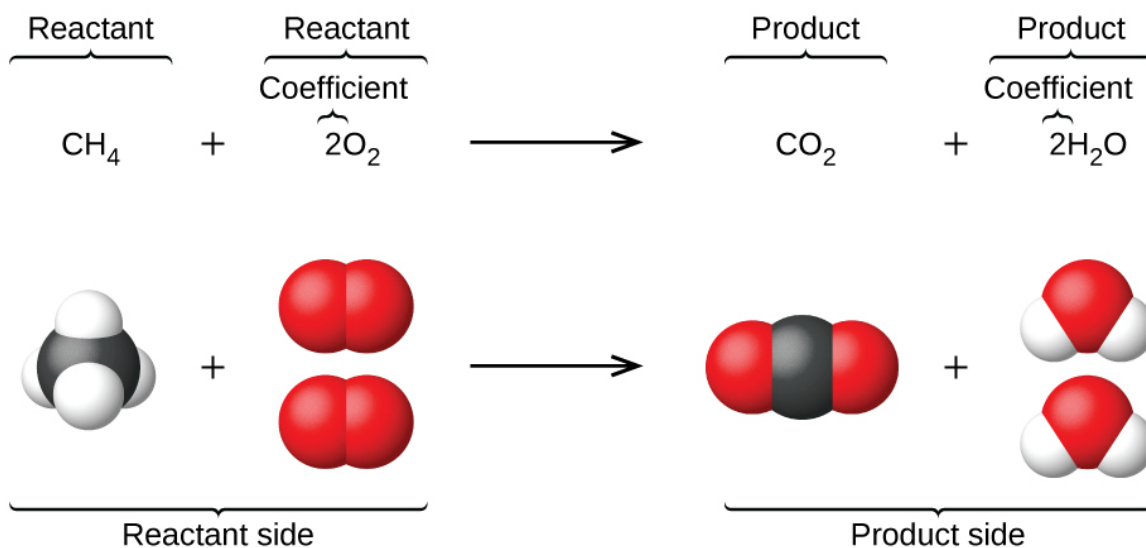
Solid-fuel rockets are a central feature in the world's space exploration programs, including the new Space Launch System being developed by the National Aeronautics and Space Administration (NASA) to replace the retired Space Shuttle fleet ([\[link\]](#)). The engines of these rockets rely on carefully prepared solid mixtures of chemicals combined in precisely measured amounts. Igniting the mixture initiates a vigorous chemical reaction that rapidly generates large amounts of gaseous products. These gases are ejected from the rocket engine through its nozzle, providing the thrust needed to propel heavy payloads into space. Both the nature of this chemical reaction and the relationships between the amounts of the substances being consumed and produced by the reaction are critically important considerations that determine the success of the technology. This chapter will describe how to symbolize chemical reactions using chemical equations, how to classify some common chemical reactions by identifying patterns of reactivity, and how to determine the quantitative relations between the amounts of substances involved in chemical reactions—that is, the reaction *stoichiometry*.

Writing and Balancing Chemical Equations

By the end of this section, you will be able to:

- Derive chemical equations from narrative descriptions of chemical reactions.
- Write and balance chemical equations in molecular, total ionic, and net ionic formats.

The preceding chapter introduced the use of element symbols to represent individual atoms. When atoms gain or lose electrons to yield ions, or combine with other atoms to form molecules, their symbols are modified or combined to generate chemical formulas that appropriately represent these species. Extending this symbolism to represent both the identities and the relative quantities of substances undergoing a chemical (or physical) change involves writing and balancing a **chemical equation**. Consider as an example the reaction between one methane molecule (CH_4) and two diatomic oxygen molecules (O_2) to produce one carbon dioxide molecule (CO_2) and two water molecules (H_2O). The chemical equation representing this process is provided in the upper half of [\[link\]](#), with space-filling molecular models shown in the lower half of the figure.



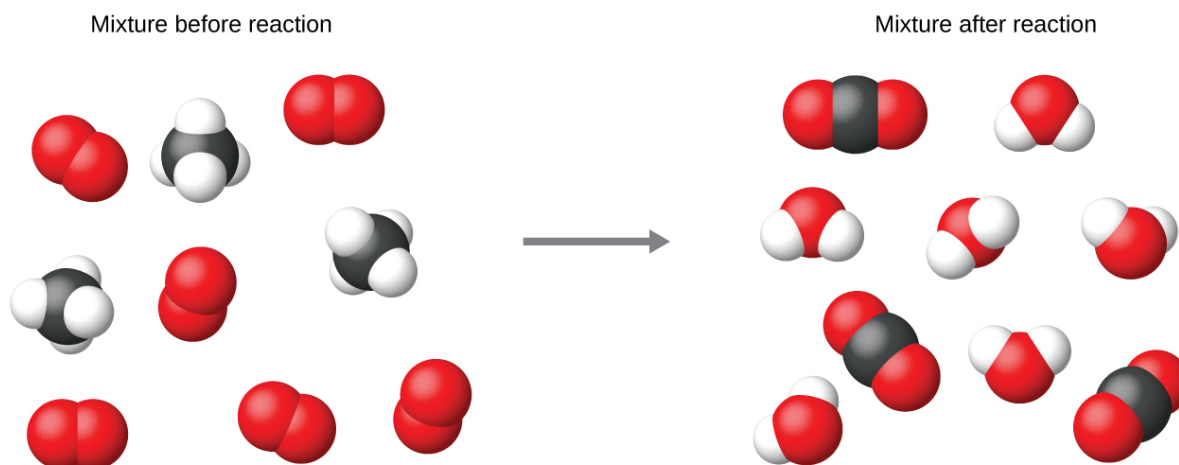
The reaction between methane and oxygen to yield carbon dioxide and water (shown at bottom) may be represented by a chemical equation using formulas (top).

This example illustrates the fundamental aspects of any chemical equation:

1. The substances undergoing reaction are called **reactants**, and their formulas are placed on the left side of the equation.
2. The substances generated by the reaction are called **products**, and their formulas are placed on the right side of the equation.
3. Plus signs (+) separate individual reactant and product formulas, and an arrow (\longrightarrow) separates the reactant and product (left and right) sides of the equation.
4. The relative numbers of reactant and product species are represented by **coefficients** (numbers placed immediately to the left of each formula). A coefficient of 1 is typically omitted.

It is common practice to use the smallest possible whole-number coefficients in a chemical equation, as is done in this example. Realize, however, that these coefficients represent the *relative* numbers of reactants and products, and, therefore, they may be correctly interpreted as ratios. Methane and oxygen react to yield carbon dioxide and water in a 1:2:1:2 ratio. This ratio is satisfied if the numbers of these molecules are, respectively, 1-2-1-2, or 2-4-2-4, or 3-6-3-6, and so on ([\[link\]](#)). Likewise, these coefficients may be interpreted with regard to any amount (number) unit, and so this equation may be correctly read in many ways, including:

- One methane molecule and two oxygen molecules react to yield one carbon dioxide molecule and two water molecules.
- One dozen methane molecules and two dozen oxygen molecules react to yield one dozen carbon dioxide molecules and two dozen water molecules.
- One mole of methane molecules and 2 moles of oxygen molecules react to yield 1 mole of carbon dioxide molecules and 2 moles of water molecules.



Regardless of the absolute numbers of molecules involved, the ratios between numbers of molecules of each species that react (the reactants) and molecules of each species that form (the products) are the same and are given by the chemical reaction equation.

Balancing Equations

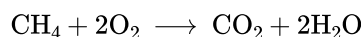
The chemical equation described in section 4.1 is **balanced**, meaning that equal numbers of atoms for each element involved in the reaction are represented on the reactant and product sides. This is a requirement the equation must satisfy to be consistent with the law of conservation of matter. It may be confirmed by simply summing the numbers of atoms on either side of the arrow and comparing these sums to ensure they are equal. Note that the number of atoms for a given element is calculated by multiplying the coefficient of any formula containing that element by the element's subscript in the formula. If an element appears in more than one formula on a given side of the equation, the number of atoms represented in each must be computed and then added together. For example, both product species in the example reaction, CO_2 and H_2O , contain the element oxygen, and so the number of oxygen atoms on the product side of the equation is

Equation:

$$\left(1 \text{ CO}_2 \text{ molecule} \times \frac{2 \text{ O atoms}}{\text{CO}_2 \text{ molecule}} \right) + \left(2 \text{ H}_2\text{O molecules} \times \frac{1 \text{ O atom}}{\text{H}_2\text{O molecule}} \right) = 4 \text{ O atoms}$$

The equation for the reaction between methane and oxygen to yield carbon dioxide and water is confirmed to be balanced per this approach, as shown here:

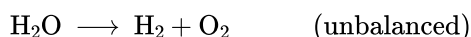
Equation:



Element	Reactants	Products	Balanced?
C	$1 \times 1 = 1$	$1 \times 1 = 1$	$1 = 1$, yes
H	$4 \times 1 = 4$	$2 \times 2 = 4$	$4 = 4$, yes
O	$2 \times 2 = 4$	$(1 \times 2) + (2 \times 1) = 4$	$4 = 4$, yes

A balanced chemical equation often may be derived from a qualitative description of some chemical reaction by a fairly simple approach known as balancing by inspection. Consider as an example the decomposition of water to yield molecular hydrogen and oxygen. This process is represented qualitatively by an *unbalanced* chemical equation:

Equation:

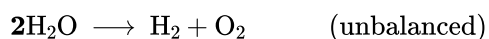


Comparing the number of H and O atoms on either side of this equation confirms its imbalance:

Element	Reactants	Products	Balanced?
H	$1 \times 2 = 2$	$1 \times 2 = 2$	$2 = 2$, yes
O	$1 \times 1 = 1$	$1 \times 2 = 2$	$1 \neq 2$, no

The numbers of H atoms on the reactant and product sides of the equation are equal, but the numbers of O atoms are not. To achieve balance, the *coefficients* of the equation may be changed as needed. Keep in mind, of course, that the *formula subscripts* define, in part, the identity of the substance, and so these cannot be changed without altering the qualitative meaning of the equation. For example, changing the reactant formula from H_2O to H_2O_2 would yield balance in the number of atoms, but doing so also changes the reactant's identity (it's now hydrogen peroxide and not water). The O atom balance may be achieved by changing the coefficient for H_2O to 2.

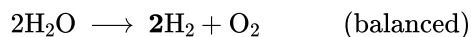
Equation:



Element	Reactants	Products	Balanced?
H	$2 \times 2 = 4$	$1 \times 2 = 2$	$4 \neq 2$, no
O	$2 \times 1 = 2$	$1 \times 2 = 2$	$2 = 2$, yes

The H atom balance was upset by this change, but it is easily reestablished by changing the coefficient for the H_2 product to 2.

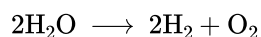
Equation:



Element	Reactants	Products	Balanced?
H	$2 \times 2 = 4$	$2 \times 2 = 4$	$4 = 4$, yes
O	$2 \times 1 = 2$	$1 \times 2 = 2$	$2 = 2$, yes

These coefficients yield equal numbers of both H and O atoms on the reactant and product sides, and the balanced equation is, therefore:

Equation:



Example:

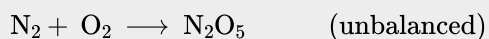
Balancing Chemical Equations

Write a balanced equation for the reaction of molecular nitrogen (N_2) and oxygen (O_2) to form dinitrogen pentoxide.

Solution

First, write the unbalanced equation.

Equation:



Next, count the number of each type of atom present in the unbalanced equation.

Element	Reactants	Products	Balanced?
N	$1 \times 2 = 2$	$1 \times 2 = 2$	$2 = 2$, yes
O	$1 \times 2 = 2$	$1 \times 5 = 5$	$2 \neq 5$, no

Though nitrogen is balanced, changes in coefficients are needed to balance the number of oxygen atoms. To balance the number of oxygen atoms, a reasonable first attempt would be to change the coefficients for the O_2 and N_2O_5 to integers that will yield 10 O atoms (the least common multiple for the O atom subscripts in these two formulas).

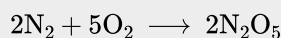
Equation:



Element	Reactants	Products	Balanced?
N	$1 \times 2 = 2$	$2 \times 2 = 4$	$2 \neq 4$, no
O	$5 \times 2 = 10$	$2 \times 5 = 10$	$10 = 10$, yes

The N atom balance has been upset by this change; it is restored by changing the coefficient for the reactant N₂ to 2.

Equation:



Element	Reactants	Products	Balanced?
N	$2 \times 2 = 4$	$2 \times 2 = 4$	$4 = 4$, yes
O	$5 \times 2 = 10$	$2 \times 5 = 10$	$10 = 10$, yes

The numbers of N and O atoms on either side of the equation are now equal, and so the equation is balanced.

Check Your Learning

Write a balanced equation for the decomposition of ammonium nitrate to form molecular nitrogen, molecular oxygen, and water. (Hint: Balance oxygen last, since it is present in more than one molecule on the right side of the equation.)

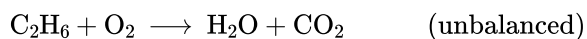
Note:

Answer:



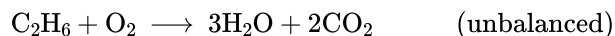
It is sometimes convenient to use fractions instead of integers as intermediate coefficients in the process of balancing a chemical equation. When balance is achieved, all the equation's coefficients may then be multiplied by a whole number to convert the fractional coefficients to integers without upsetting the atom balance. For example, consider the reaction of ethane (C₂H₆) with oxygen to yield H₂O and CO₂, represented by the unbalanced equation:

Equation:



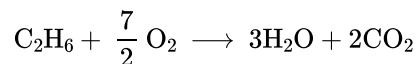
Following the usual inspection approach, one might first balance C and H atoms by changing the coefficients for the two product species, as shown:

Equation:



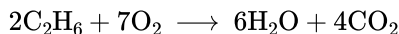
This results in seven O atoms on the product side of the equation, an odd number—no integer coefficient can be used with the O₂ reactant to yield an odd number, so a fractional coefficient, $\frac{7}{2}$, is used instead to yield a provisional balanced equation:

Equation:



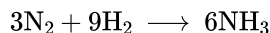
A conventional balanced equation with integer-only coefficients is derived by multiplying each coefficient by 2:

Equation:



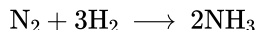
Finally with regard to balanced equations, recall that convention dictates use of the *smallest whole-number coefficients*. Although the equation for the reaction between molecular nitrogen and molecular hydrogen to produce ammonia is, indeed, balanced,

Equation:



the coefficients are not the smallest possible integers representing the relative numbers of reactant and product molecules. Dividing each coefficient by the greatest common factor, 3, gives the preferred equation:

Equation:



Note:

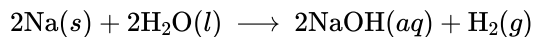


Use this interactive [tutorial](#) for additional practice balancing equations.

Additional Information in Chemical Equations

The physical states of reactants and products in chemical equations very often are indicated with a parenthetical abbreviation following the formulas. Common abbreviations include *s* for solids, *l* for liquids, *g* for gases, and *aq* for substances dissolved in water (*aqueous solutions*, as introduced in the preceding chapter). These notations are illustrated in the example equation here:

Equation:

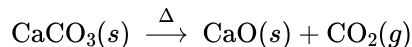


This equation represents the reaction that takes place when sodium metal is placed in water. The solid sodium reacts with liquid water to produce molecular hydrogen gas and the ionic compound sodium hydroxide (a solid in

pure form, but readily dissolved in water).

Special conditions necessary for a reaction are sometimes designated by writing a word or symbol above or below the equation's arrow. For example, a reaction carried out by heating may be indicated by the uppercase Greek letter delta (Δ) over the arrow.

Equation:

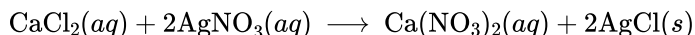


Other examples of these special conditions will be encountered in more depth in later chapters.

Equations for Ionic Reactions

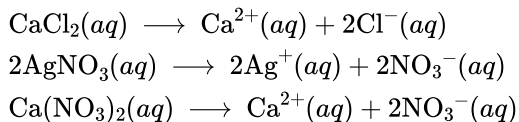
Given the abundance of water on earth, it stands to reason that a great many chemical reactions take place in aqueous media. When ions are involved in these reactions, the chemical equations may be written with various levels of detail appropriate to their intended use. To illustrate this, consider a reaction between ionic compounds taking place in an aqueous solution. When aqueous solutions of CaCl_2 and AgNO_3 are mixed, a reaction takes place producing aqueous $\text{Ca}(\text{NO}_3)_2$ and solid AgCl :

Equation:



This balanced equation, derived in the usual fashion, is called a **molecular equation** because it doesn't explicitly represent the ionic species that are present in solution. When ionic compounds dissolve in water, they may *dissociate* into their constituent ions, which are subsequently dispersed homogeneously throughout the resulting solution (a thorough discussion of this important process is provided in the chapter on solutions). Ionic compounds dissolved in water are, therefore, more realistically represented as dissociated ions, in this case:

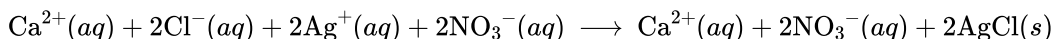
Equation:



Unlike these three ionic compounds, AgCl does not dissolve in water to a significant extent, as signified by its physical state notation, s .

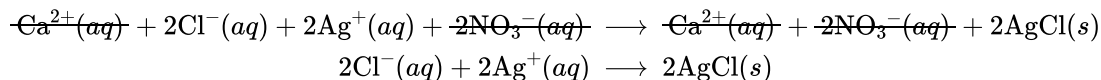
Explicitly representing all dissolved ions results in a **complete ionic equation**. In this particular case, the formulas for the dissolved ionic compounds are replaced by formulas for their dissociated ions:

Equation:



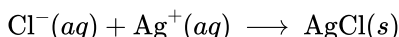
Examining this equation shows that two chemical species are present in identical form on both sides of the arrow, $\text{Ca}^{2+}(aq)$ and $\text{NO}_3^{-}(aq)$. These **spectator ions**—ions whose presence is required to maintain charge neutrality—are neither chemically nor physically changed by the process, and so they may be eliminated from the equation to yield a more succinct representation called a **net ionic equation**:

Equation:



Following the convention of using the smallest possible integers as coefficients, this equation is then written:

Equation:



This net ionic equation indicates that solid silver chloride may be produced from dissolved chloride and silver(I) ions, regardless of the source of these ions. These molecular and complete ionic equations provide additional information, namely, the ionic compounds used as sources of Cl^{-} and Ag^{+} .

Example:

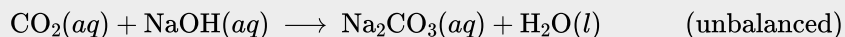
Molecular and Ionic Equations

When carbon dioxide is dissolved in an aqueous solution of sodium hydroxide, the mixture reacts to yield aqueous sodium carbonate and liquid water. Write balanced molecular, complete ionic, and net ionic equations for this process.

Solution

Begin by identifying formulas for the reactants and products and arranging them properly in chemical equation form:

Equation:



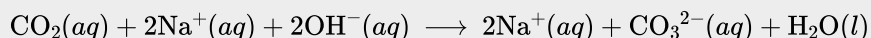
Balance is achieved easily in this case by changing the coefficient for NaOH to 2, resulting in the molecular equation for this reaction:

Equation:



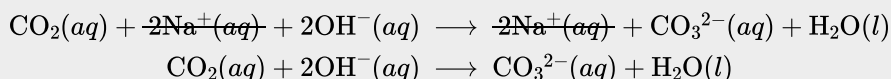
The two dissolved ionic compounds, NaOH and Na_2CO_3 , can be represented as dissociated ions to yield the complete ionic equation:

Equation:



Finally, identify the spectator ion(s), in this case $\text{Na}^{+}(aq)$, and remove it from each side of the equation to generate the net ionic equation:

Equation:



Check Your Learning

Diatomic chlorine and sodium hydroxide (lye) are commodity chemicals produced in large quantities, along with diatomic hydrogen, via the electrolysis of brine, according to the following unbalanced equation:

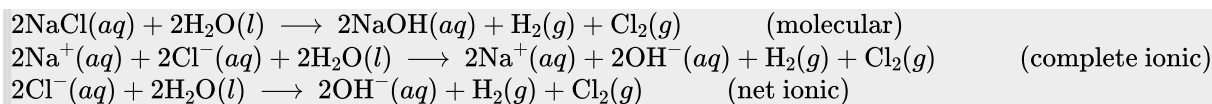
Equation:



Write balanced molecular, complete ionic, and net ionic equations for this process.

Note:

Answer:



Key Concepts and Summary

Chemical equations are symbolic representations of chemical and physical changes. Formulas for the substances undergoing the change (reactants) and substances generated by the change (products) are separated by an arrow and preceded by integer coefficients indicating their relative numbers. Balanced equations are those whose coefficients result in equal numbers of atoms for each element in the reactants and products. Chemical reactions in aqueous solution that involve ionic reactants or products may be represented more realistically by complete ionic equations and, more succinctly, by net ionic equations.

Chemistry End of Chapter Exercises

Exercise:

Problem:

What does it mean to say an equation is balanced? Why is it important for an equation to be balanced?

Solution:

An equation is balanced when the same number of each element is represented on the reactant and product sides. Equations must be balanced to accurately reflect the law of conservation of matter.

Exercise:

Problem: Consider molecular, complete ionic, and net ionic equations.

- What is the difference between these types of equations?
- In what circumstance would the complete and net ionic equations for a reaction be identical?

Exercise:

Problem: Balance the following equations:

- $\text{PCl}_5(s) + \text{H}_2\text{O}(l) \longrightarrow \text{POCl}_3(l) + \text{HCl}(aq)$
- $\text{Cu}(s) + \text{HNO}_3(aq) \longrightarrow \text{Cu}(\text{NO}_3)_2(aq) + \text{H}_2\text{O}(l) + \text{NO}(g)$
- $\text{H}_2(g) + \text{I}_2(s) \longrightarrow \text{HI}(s)$
- $\text{Fe}(s) + \text{O}_2(g) \longrightarrow \text{Fe}_2\text{O}_3(s)$
- $\text{Na}(s) + \text{H}_2\text{O}(l) \longrightarrow \text{NaOH}(aq) + \text{H}_2(g)$
- $(\text{NH}_4)_2\text{Cr}_2\text{O}_7(s) \longrightarrow \text{Cr}_2\text{O}_3(s) + \text{N}_2(g) + \text{H}_2\text{O}(g)$
- $\text{P}_4(s) + \text{Cl}_2(g) \longrightarrow \text{PCl}_3(l)$
- $\text{PtCl}_4(s) \longrightarrow \text{Pt}(s) + \text{Cl}_2(g)$

Solution:

(a) $\text{PCl}_5(s) + \text{H}_2\text{O}(l) \longrightarrow \text{POCl}_3(l) + 2\text{HCl}(aq)$; (b) $3\text{Cu}(s) + 8\text{HNO}_3(aq) \longrightarrow 3\text{Cu}(\text{NO}_3)_2(aq) + 4\text{H}_2\text{O}(l) + 2\text{NO}(g)$; (c) $\text{H}_2(g) + \text{I}_2(s) \longrightarrow 2\text{HI}(s)$; (d) $4\text{Fe}(s) + 3\text{O}_2(g) \longrightarrow 2\text{Fe}_2\text{O}_3(s)$; (e) $2\text{Na}(s) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{NaOH}(aq) + \text{H}_2(g)$; (f) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7(s) \longrightarrow \text{Cr}_2\text{O}_3(s) + \text{N}_2(g) + 4\text{H}_2\text{O}(g)$; (g) $\text{P}_4(s) + 6\text{Cl}_2(g) \longrightarrow 4\text{PCl}_3(l)$; (h) $\text{PtCl}_4(s) \longrightarrow \text{Pt}(s) + 2\text{Cl}_2(g)$

Exercise:

Problem: Balance the following equations:

- (a) $\text{Ag}(s) + \text{H}_2\text{S}(g) + \text{O}_2(g) \longrightarrow \text{Ag}_2\text{S}(s) + \text{H}_2\text{O}(l)$
(b) $\text{P}_4(s) + \text{O}_2(g) \longrightarrow \text{P}_4\text{O}_{10}(s)$
(c) $\text{Pb}(s) + \text{H}_2\text{O}(l) + \text{O}_2(g) \longrightarrow \text{Pb}(\text{OH})_2(s)$
(d) $\text{Fe}(s) + \text{H}_2\text{O}(l) \longrightarrow \text{Fe}_3\text{O}_4(s) + \text{H}_2(g)$
(e) $\text{Sc}_2\text{O}_3(s) + \text{SO}_3(l) \longrightarrow \text{Sc}_2(\text{SO}_4)_3(s)$
(f) $\text{Ca}_3(\text{PO}_4)_2(aq) + \text{H}_3\text{PO}_4(aq) \longrightarrow \text{Ca}(\text{H}_2\text{PO}_4)_2(aq)$
(g) $\text{Al}(s) + \text{H}_2\text{SO}_4(aq) \longrightarrow \text{Al}_2(\text{SO}_4)_3(s) + \text{H}_2(g)$
(h) $\text{TiCl}_4(s) + \text{H}_2\text{O}(g) \longrightarrow \text{TiO}_2(s) + \text{HCl}(g)$

Exercise:

Problem: Write a balanced molecular equation describing each of the following chemical reactions.

- (a) Solid calcium carbonate is heated and decomposes to solid calcium oxide and carbon dioxide gas.
(b) Gaseous butane, C_4H_{10} , reacts with diatomic oxygen gas to yield gaseous carbon dioxide and water vapor.
(c) Aqueous solutions of magnesium chloride and sodium hydroxide react to produce solid magnesium hydroxide and aqueous sodium chloride.
(d) Water vapor reacts with sodium metal to produce solid sodium hydroxide and hydrogen gas.

Solution:

(a) $\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$; (b) $2\text{C}_4\text{H}_{10}(g) + 13\text{O}_2(g) \longrightarrow 8\text{CO}_2(g) + 10\text{H}_2\text{O}(g)$; (c) $\text{MgCl}_2(aq) + 2\text{NaOH}(aq) \longrightarrow \text{Mg}(\text{OH})_2(s) + 2\text{NaCl}(aq)$; (d) $2\text{H}_2\text{O}(g) + 2\text{Na}(s) \longrightarrow 2\text{NaOH}(s) + \text{H}_2(g)$

Exercise:

Problem: Write a balanced equation describing each of the following chemical reactions.

- (a) Solid potassium chlorate, KClO_3 , decomposes to form solid potassium chloride and diatomic oxygen gas.
(b) Solid aluminum metal reacts with solid diatomic iodine to form solid Al_2I_6 .
(c) When solid sodium chloride is added to aqueous sulfuric acid, hydrogen chloride gas and aqueous sodium sulfate are produced.

(d) Aqueous solutions of phosphoric acid and potassium hydroxide react to produce aqueous potassium dihydrogen phosphate and liquid water.

Exercise:

Problem:

Colorful fireworks often involve the decomposition of barium nitrate and potassium chlorate and the reaction of the metals magnesium, aluminum, and iron with oxygen.

(a) Write the formulas of barium nitrate and potassium chlorate.

(b) The decomposition of solid potassium chlorate leads to the formation of solid potassium chloride and diatomic oxygen gas. Write an equation for the reaction.

(c) The decomposition of solid barium nitrate leads to the formation of solid barium oxide, diatomic nitrogen gas, and diatomic oxygen gas. Write an equation for the reaction.

(d) Write separate equations for the reactions of the solid metals magnesium, aluminum, and iron with diatomic oxygen gas to yield the corresponding metal oxides. (Assume the iron oxide contains Fe^{3+} ions.)

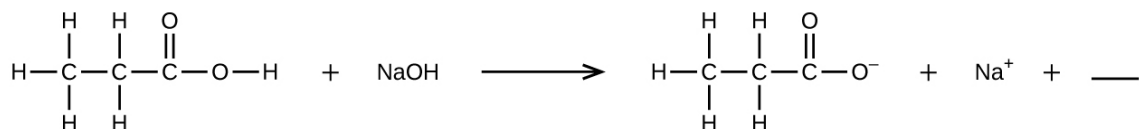
Solution:

(a) $\text{Ba}(\text{NO}_3)_2$, KClO_3 ; (b) $2\text{KClO}_3(s) \rightarrow 2\text{KCl}(s) + 3\text{O}_2(g)$; (c) $2\text{Ba}(\text{NO}_3)_2(s) \rightarrow 2\text{BaO}(s) + 2\text{N}_2(g) + 5\text{O}_2(g)$; (d) $2\text{Mg}(s) + \text{O}_2(g) \rightarrow 2\text{MgO}(s)$; $4\text{Al}(s) + 3\text{O}_2(g) \rightarrow 2\text{Al}_2\text{O}_3(s)$; $4\text{Fe}(s) + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)$

Exercise:

Problem:

Fill in the blank with a single chemical formula for a covalent compound that will balance the equation:



Exercise:

Problem:

Aqueous hydrogen fluoride (hydrofluoric acid) is used to etch glass and to analyze minerals for their silicon content. Hydrogen fluoride will also react with sand (silicon dioxide).

(a) Write an equation for the reaction of solid silicon dioxide with hydrofluoric acid to yield gaseous silicon tetrafluoride and liquid water.

(b) The mineral fluorite (calcium fluoride) occurs extensively in Illinois. Solid calcium fluoride can also be prepared by the reaction of aqueous solutions of calcium chloride and sodium fluoride, yielding aqueous sodium chloride as the other product. Write complete and net ionic equations for this reaction.

Solution:

(a) $4\text{HF}(aq) + \text{SiO}_2(s) \rightarrow \text{SiF}_4(g) + 2\text{H}_2\text{O}(l)$; (b) complete ionic equation:
 $2\text{Na}^+(aq) + 2\text{F}^-(aq) + \text{Ca}^{2+}(aq) + 2\text{Cl}^-(aq) \rightarrow \text{CaF}_2(s) + 2\text{Na}^+(aq) + 2\text{Cl}^-(aq)$, net ionic equation: $2\text{F}^-(aq) + \text{Ca}^{2+}(aq) \rightarrow \text{CaF}_2(s)$

Exercise:

Problem:

A novel process for obtaining magnesium from sea water involves several reactions. Write a balanced chemical equation for each step of the process.

(a) The first step is the decomposition of solid calcium carbonate from seashells to form solid calcium oxide and gaseous carbon dioxide.

(b) The second step is the formation of solid calcium hydroxide as the only product from the reaction of the solid calcium oxide with liquid water.

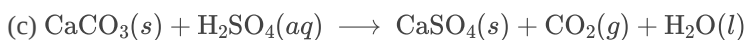
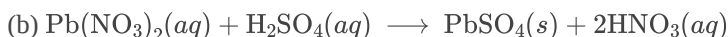
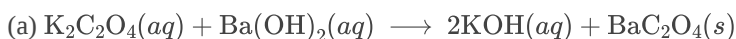
(c) Solid calcium hydroxide is then added to the seawater, reacting with dissolved magnesium chloride to yield solid magnesium hydroxide and aqueous calcium chloride.

(d) The solid magnesium hydroxide is added to a hydrochloric acid solution, producing dissolved magnesium chloride and liquid water.

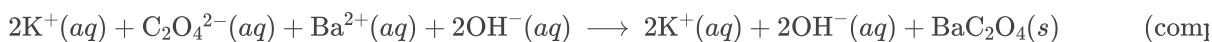
(e) Finally, the magnesium chloride is melted and electrolyzed to yield liquid magnesium metal and diatomic chlorine gas.

Exercise:**Problem:**

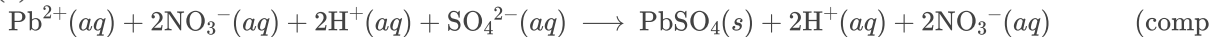
From the balanced molecular equations, write the complete ionic and net ionic equations for the following:

**Solution:**

(a)



(b)

**Glossary**

balanced equation

chemical equation with equal numbers of atoms for each element in the reactant and product

chemical equation

symbolic representation of a chemical reaction

coefficient

number placed in front of symbols or formulas in a chemical equation to indicate their relative amount

complete ionic equation

chemical equation in which all dissolved ionic reactants and products, including spectator ions, are explicitly represented by formulas for their dissociated ions

molecular equation

chemical equation in which all reactants and products are represented as neutral substances

net ionic equation

chemical equation in which only those dissolved ionic reactants and products that undergo a chemical or physical change are represented (excludes spectator ions)

product

substance formed by a chemical or physical change; shown on the right side of the arrow in a chemical equation

reactant

substance undergoing a chemical or physical change; shown on the left side of the arrow in a chemical equation

spectator ion

ion that does not undergo a chemical or physical change during a reaction, but its presence is required to maintain charge neutrality

Introduction

class="introduction"

- Gas Pressure
- Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law
- Stoichiometry of Gaseous Substances, Mixtures, and Reactions
- Effusion and Diffusion of Gases
- The Kinetic-Molecular Theory
- Non-Ideal Gas Behavior

The hot air
inside these
balloons is
less dense
than the
surrounding
cool air.

This results
in a buoyant
force that
causes the
balloons to
rise when
their guy
lines are
untied.

(credit:
modification
of work
by Anthony
Quintano)



We are surrounded by an ocean of gas—the atmosphere—and many of the properties of gases are familiar to us from our daily activities. Heated gases expand, which can make a hot air balloon rise ([\[link\]](#)) or cause a blowout in a bicycle tire left in the sun on a hot day.

Gases have played an important part in the development of chemistry. In the seventeenth and eighteenth centuries, many scientists investigated gas behavior, providing the first mathematical descriptions of the behavior of matter.

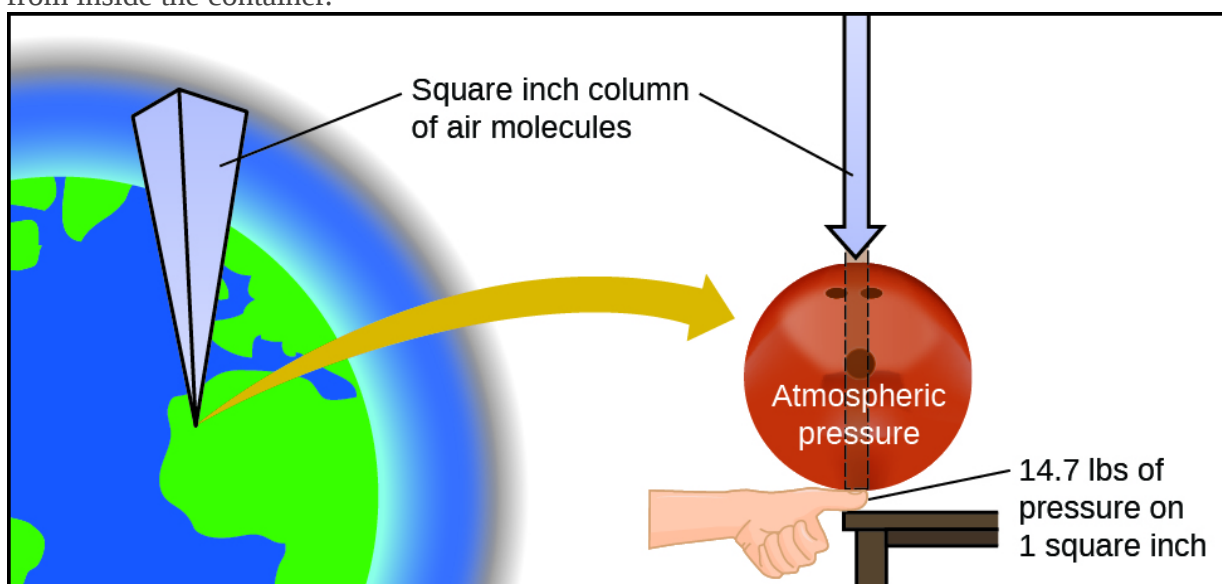
In this chapter, we will examine the relationships between gas temperature, pressure, amount, and volume. We will study a simple theoretical model and use it to analyze the experimental behavior of gases. The results of these analyses will show us the limitations of the theory and how to improve on it.

Gas Pressure

By the end of this section, you will be able to:

- Define the property of pressure
- Define and convert among the units of pressure measurements
- Describe the operation of common tools for measuring gas pressure
- Calculate pressure from manometer data

The earth's atmosphere exerts a pressure, as does any other gas. Although we do not normally notice atmospheric pressure, we are sensitive to pressure changes—for example, when your ears “pop” during take-off and landing while flying, or when you dive underwater. Gas pressure is caused by the force exerted by gas molecules colliding with the surfaces of objects ([link](#)). Although the force of each collision is very small, any surface of appreciable area experiences a large number of collisions in a short time, which can result in a high pressure. In fact, normal air pressure is strong enough to crush a metal container when not balanced by equal pressure from inside the container.



The atmosphere above us exerts a large pressure on objects at the surface of the earth, roughly equal to the weight of a bowling ball pressing on an area the size of a human thumbnail.

Note:



A dramatic [illustration](#) of atmospheric pressure is provided in this brief video, which shows a railway tanker car imploding when its internal pressure is decreased. A smaller scale [demonstration](#) of this phenomenon is briefly explained.

Atmospheric pressure is caused by the weight of the column of air molecules in the atmosphere above an object, such as the tanker car. At sea level, this pressure is roughly the same as that exerted by a full-grown African elephant standing on a doormat, or a typical bowling ball resting on your thumbnail. These may seem like huge amounts, and they are, but life on earth has evolved under such atmospheric pressure. If you actually perch a bowling ball on your thumbnail, the pressure experienced is *twice* the usual pressure, and the sensation is unpleasant.

In general, **pressure** is defined as the force exerted on a given area: $P = \frac{F}{A}$. Note that pressure is directly proportional to force and inversely proportional to area. Thus, pressure can be increased either by increasing the amount of force or by decreasing the area over which it is applied; pressure can be decreased by decreasing the force or increasing the area.

Let's apply this concept to determine which would be more likely to fall through thin ice in [\[link\]](#)—the elephant or the figure skater? A large African elephant can weigh 7 tons, supported on four feet, each with a diameter of about 1.5 ft (footprint area of 250 in²), so the pressure exerted by each foot is about 14 lb/in²:

Equation:

$$\text{pressure per elephant foot} = 14,000 \frac{\text{lb}}{\text{elephant}} \times \frac{1 \text{ elephant}}{4 \text{ feet}} \times \frac{1 \text{ foot}}{250 \text{ in}^2} = 14 \text{ lb/in}^2$$

The figure skater weighs about 120 lbs, supported on two skate blades, each with an area of about 2 in², so the pressure exerted by each blade is about 30 lb/in²:

Equation:

$$\text{pressure per skate blade} = 120 \frac{\text{lb}}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ blades}} \times \frac{1 \text{ blade}}{2 \text{ in}^2} = 30 \text{ lb/in}^2$$

Even though the elephant is more than one hundred-times heavier than the skater, it exerts less than one-half of the pressure and would therefore be less likely to fall through thin ice. On the other hand, if the skater removes her skates and stands with bare feet (or regular footwear) on the ice, the larger area over which her weight is applied greatly reduces the pressure exerted:

Equation:

$$\text{pressure per human foot} = 120 \frac{\text{lb}}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ feet}} \times \frac{1 \text{ foot}}{30 \text{ in}^2} = 2 \text{ lb/in}^2$$



(a)



(b)

Although (a) an elephant’s weight is large, creating a very large force on the ground, (b) the figure skater exerts a much higher pressure on the ice due to the small surface area of her skates. (credit a: modification of work by Guido da Rozze; credit b: modification of work by Ryosuke Yagi)

The SI unit of pressure is the **pascal (Pa)**, with $1 \text{ Pa} = 1 \text{ N/m}^2$, where N is the newton, a unit of force defined as 1 kg m/s^2 . One pascal is a small pressure; in many cases, it is more convenient to use units of kilopascal ($1 \text{ kPa} = 1000 \text{ Pa}$) or **bar** ($1 \text{ bar} = 100,000 \text{ Pa}$). In the United States, pressure is often measured in pounds of force on an area of one square inch—**pounds per square inch (psi)**—for example, in car tires. Pressure can also be measured using the unit **atmosphere (atm)**, which originally represented the average sea level air pressure at the approximate latitude of Paris (45°). [\[link\]](#) provides some information on these and a few other common units for pressure measurements

Pressure Units	
Unit Name and Abbreviation	Definition or Relation to Other Unit

Pressure Units	
Unit Name and Abbreviation	Definition or Relation to Other Unit
pascal (Pa)	1 Pa = 1 N/m ² recommended IUPAC unit
kilopascal (kPa)	1 kPa = 1000 Pa
pounds per square inch (psi)	air pressure at sea level is ~14.7 psi
atmosphere (atm)	1 atm = 101,325 Pa air pressure at sea level is ~1 atm
bar (bar, or b)	1 bar = 100,000 Pa (exactly) commonly used in meteorology
millibar (mbar, or mb)	1000 mbar = 1 bar
inches of mercury (in. Hg)	1 in. Hg = 3386 Pa used by aviation industry, also some weather reports
torr	1 torr = $\frac{1}{760}$ atm named after Evangelista Torricelli, inventor of the barometer
millimeters of mercury (mm Hg)	1 mm Hg ~1 torr

Example:

Conversion of Pressure Units

The United States National Weather Service reports pressure in both inches of Hg and millibars. Convert a pressure of 29.2 in. Hg into:

- (a) torr
- (b) atm
- (c) kPa
- (d) mbar

Solution

This is a unit conversion problem. The relationships between the various pressure units are given in [\[link\]](#).

$$(a) 29.2 \text{ in. Hg} \times \frac{25.4 \text{ mm}}{1 \text{ in.}} \times \frac{1 \text{ torr}}{1 \text{ mm Hg}} = 742 \text{ torr}$$

$$(b) 742 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.976 \text{ atm}$$

$$(c) 742 \text{ torr} \times \frac{101.325 \text{ kPa}}{760 \text{ torr}} = 98.9 \text{ kPa}$$

$$(d) 98.9 \text{ kPa} \times \frac{1000 \text{ Pa}}{1 \text{ kPa}} \times \frac{1 \text{ bar}}{100,000 \text{ Pa}} \times \frac{1000 \text{ mbar}}{1 \text{ bar}} = 989 \text{ mbar}$$

Check Your Learning

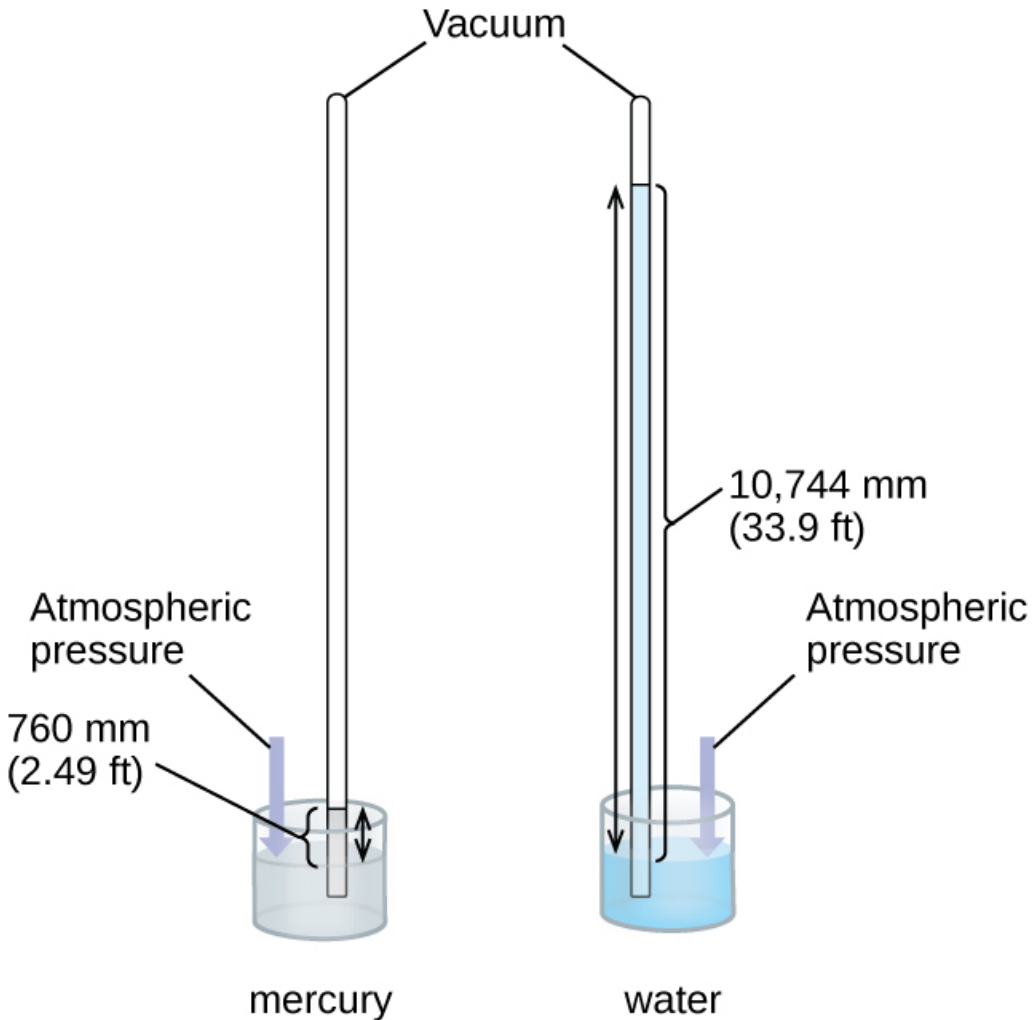
A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimeters of mercury, in kilopascals, and in bar?

Note:

Answer:

0.974 atm; 740 mm Hg; 98.7 kPa; 0.987 bar

We can measure atmospheric pressure, the force exerted by the atmosphere on the earth's surface, with a **barometer** ([link](#)). A barometer is a glass tube that is closed at one end, filled with a nonvolatile liquid such as mercury, and then inverted and immersed in a container of that liquid. The atmosphere exerts pressure on the liquid outside the tube, the column of liquid exerts pressure inside the tube, and the pressure at the liquid surface is the same inside and outside the tube. The height of the liquid in the tube is therefore proportional to the pressure exerted by the atmosphere.



In a barometer, the height, h , of the column of liquid is used as a measurement of the air pressure. Using very dense liquid mercury (left) permits the construction of reasonably sized barometers, whereas using water (right) would require a barometer more than 30 feet tall.

If the liquid is water, normal atmospheric pressure will support a column of water over 10 meters high, which is rather inconvenient for making (and reading) a barometer. Because mercury (Hg) is about 13.6-times denser than water, a mercury barometer only needs to be $\frac{1}{13.6}$ as tall as a water barometer—a more suitable size. Standard atmospheric pressure of 1 atm at sea level (101,325 Pa) corresponds to a column of mercury that is about 760 mm (29.92 in.) high. The **torr** was originally intended to be a unit equal to one millimeter of mercury, but it no longer corresponds exactly. The pressure exerted by a fluid due to gravity is known as **hydrostatic pressure**, p :

Equation:

$$p = h\rho g$$

where h is the height of the fluid, ρ is the density of the fluid, and g is acceleration due to gravity.

Example:

Calculation of Barometric Pressure

Show the calculation supporting the claim that atmospheric pressure near sea level corresponds to the pressure exerted by a column of mercury that is about 760 mm high. The density of mercury = 13.6 g/cm³.

Solution

The hydrostatic pressure is given by $p = h\rho g$, with $h = 760$ mm, $\rho = 13.6$ g/cm³, and $g = 9.81$ m/s². Plugging these values into the equation and doing the necessary unit conversions will give us the value we seek. (Note: We are expecting to find a pressure of ~101,325 Pa.)

Equation:

$$101,325 \text{ N/m}^2 = 101,325 \frac{\text{kg}\cdot\text{m/s}^2}{\text{m}^2} = 101,325 \frac{\text{kg}}{\text{m}\cdot\text{s}^2}$$

Equation:

$$p = \left(760 \text{ mm} \times \frac{1 \text{ m}}{1000 \text{ mm}} \right) \times \left(\frac{13.6 \text{ g}}{1 \text{ cm}^3} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{(100 \text{ cm})^3}{(1 \text{ m})^3} \right) \times \left(\frac{9.81 \text{ m}}{1 \text{ s}^2} \right)$$

Equation:

$$= (0.760 \text{ m}) \left(13,600 \text{ kg/m}^3 \right) \left(9.81 \text{ m/s}^2 \right) = 1.01 \times 10^5 \text{ kg/ms}^2 = 1.01 \times 10^5 \text{ N/m}^2$$

Equation:

$$= 1.01 \times 10^5 \text{ Pa}$$

Check Your Learning

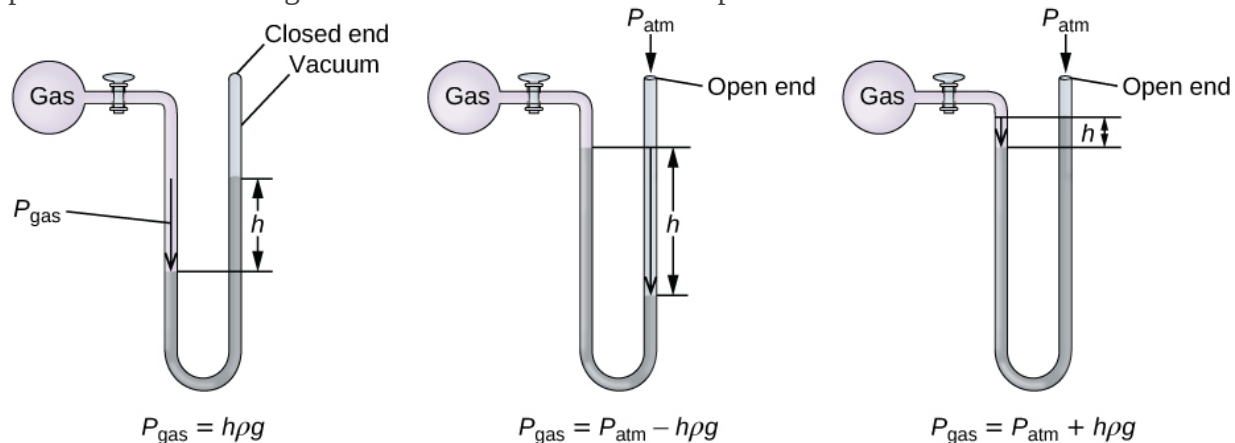
Calculate the height of a column of water at 25 °C that corresponds to normal atmospheric pressure. The density of water at this temperature is 1.0 g/cm³.

Note:

Answer:

10.3 m

A **manometer** is a device similar to a barometer that can be used to measure the pressure of a gas trapped in a container. A closed-end manometer is a U-shaped tube with one closed arm, one arm that connects to the gas to be measured, and a nonvolatile liquid (usually mercury) in between. As with a barometer, the distance between the liquid levels in the two arms of the tube (h in the diagram) is proportional to the pressure of the gas in the container. An open-end manometer ([link](#)) is the same as a closed-end manometer, but one of its arms is open to the atmosphere. In this case, the distance between the liquid levels corresponds to the difference in pressure between the gas in the container and the atmosphere.



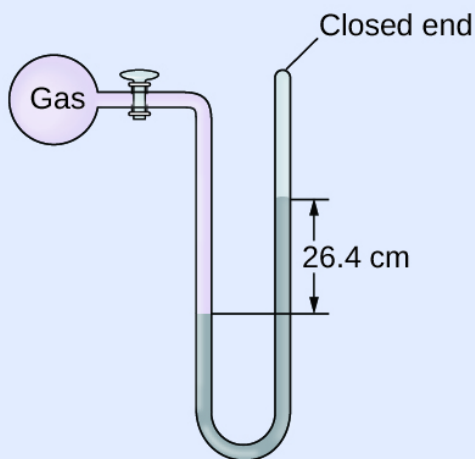
A manometer can be used to measure the pressure of a gas. The (difference in) height between the liquid levels (h) is a measure of the pressure. Mercury is usually used because of its large density.

Example:

Calculation of Pressure Using a Closed-End Manometer

The pressure of a sample of gas is measured with a closed-end manometer, as shown to the right. The liquid in the manometer is mercury. Determine the pressure of the gas in:

- (a) torr
- (b) Pa
- (c) bar



Solution

The pressure of the gas is equal to a column of mercury of height 26.4 cm. (The pressure at the bottom horizontal line is equal on both sides of the tube. The pressure on the left is due to the gas and the pressure on the right is due to 26.4 cm Hg, or mercury.) We could use the equation $p = h\rho g$ as in [\[link\]](#), but it is simpler to just convert between units using [\[link\]](#).

$$(a) \cancel{26.4 \text{ cm Hg}} \times \frac{10 \cancel{\text{ mm Hg}}}{1 \cancel{\text{ cm Hg}}} \times \frac{1 \text{ torr}}{1 \cancel{\text{ mm Hg}}} = 264 \text{ torr}$$

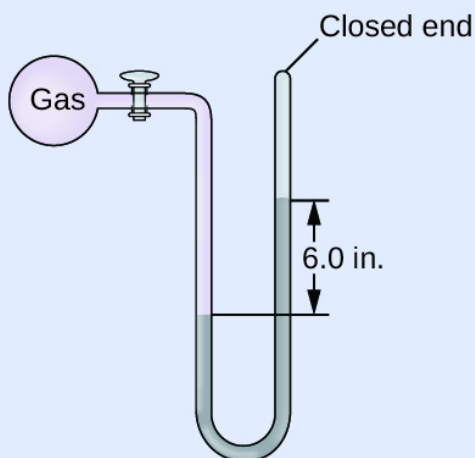
$$(b) \cancel{264 \text{ torr}} \times \frac{1 \cancel{\text{ atm}}}{760 \cancel{\text{ torr}}} \times \frac{101,325 \text{ Pa}}{1 \cancel{\text{ atm}}} = 35,200 \text{ Pa}$$

$$(c) \cancel{35,200 \text{ Pa}} \times \frac{1 \text{ bar}}{100,000 \cancel{\text{ Pa}}} = 0.352 \text{ bar}$$

Check Your Learning

The pressure of a sample of gas is measured with a closed-end manometer. The liquid in the manometer is mercury. Determine the pressure of the gas in:

- (a) torr
- (b) Pa
- (c) bar



Note:

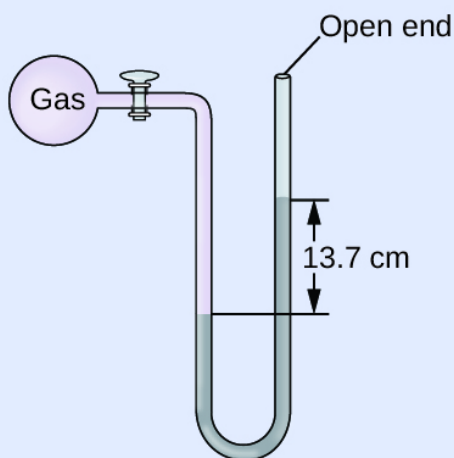
Answer:

(a) ~150 torr; (b) ~20,000 Pa; (c) ~0.20 bar

Example:**Calculation of Pressure Using an Open-End Manometer**

The pressure of a sample of gas is measured at sea level with an open-end Hg (mercury) manometer, as shown to the right. Determine the pressure of the gas in:

- (a) mm Hg
- (b) atm
- (c) kPa

**Solution**

The pressure of the gas equals the hydrostatic pressure due to a column of mercury of height 13.7 cm plus the pressure of the atmosphere at sea level. (The pressure at the bottom horizontal line is equal on both sides of the tube. The pressure on the left is due to the gas and the pressure on the right is due to 13.7 cm of Hg plus atmospheric pressure.)

(a) In mm Hg, this is: 137 mm Hg + 760 mm Hg = 897 mm Hg

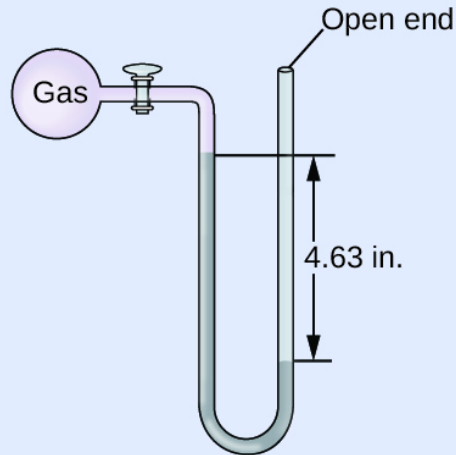
(b) $897 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = 1.18 \text{ atm}$

(c) $1.18 \text{ atm} \times \frac{101.325 \text{ kPa}}{1 \text{ atm}} = 1.20 \times 10^2 \text{ kPa}$

Check Your Learning

The pressure of a sample of gas is measured at sea level with an open-end Hg manometer, as shown to the right. Determine the pressure of the gas in:

- (a) mm Hg
- (b) atm
- (c) kPa



Note:

Answer:

(a) 642 mm Hg; (b) 0.845 atm; (c) 85.6 kPa

Note:

Measuring Blood Pressure

Blood pressure is measured using a device called a sphygmomanometer (Greek *sphygmos* = “pulse”). It consists of an inflatable cuff to restrict blood flow, a manometer to measure the pressure, and a method of determining when blood flow begins and when it becomes impeded ([link](#)). Since its invention in 1881, it has been an essential medical device. There are many types of sphygmomanometers: manual ones that require a stethoscope and are used by medical professionals; mercury ones, used when the most accuracy is required; less accurate mechanical ones; and digital ones that can be used with little training but that have limitations. When using a sphygmomanometer, the cuff is placed around the upper arm and inflated until blood flow is completely blocked, then slowly released. As the heart beats, blood forced through the arteries causes a rise in pressure. This rise in pressure at which blood flow begins is the *systolic pressure*—the peak pressure in the cardiac cycle. When the cuff’s pressure equals the arterial systolic pressure, blood flows past the cuff, creating audible sounds that can be heard using a stethoscope. This is followed by a decrease in pressure as the heart’s ventricles prepare for another beat. As cuff pressure continues to decrease, eventually sound is no longer heard; this is the *diastolic pressure*—the lowest pressure (resting phase) in the cardiac cycle. Blood pressure units from a sphygmomanometer are in terms of millimeters of mercury (mm Hg).



(a)



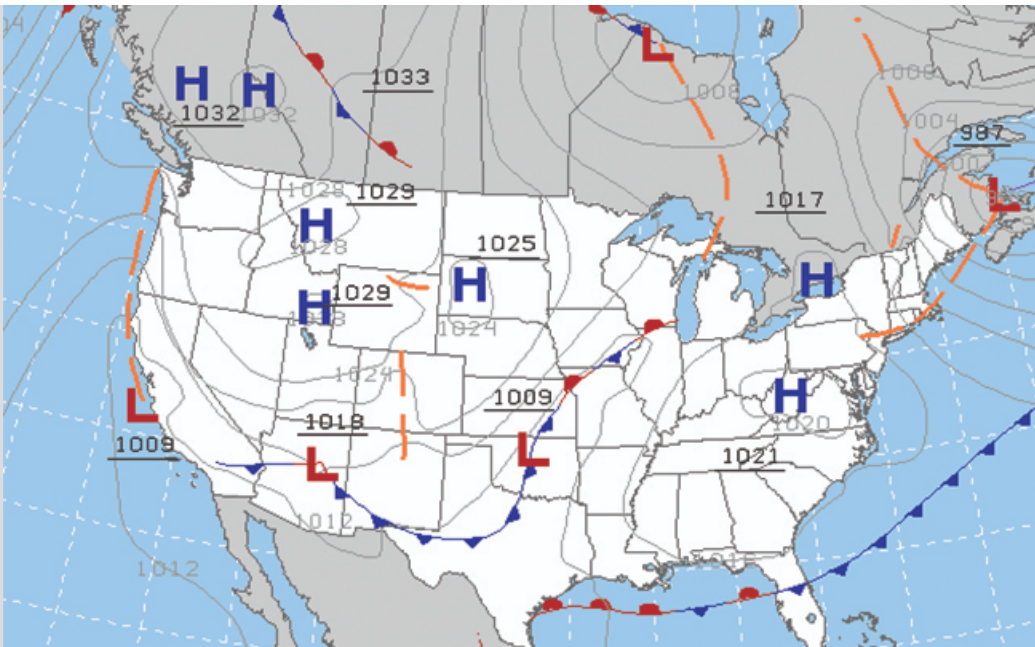
(b)

(a) A medical technician prepares to measure a patient's blood pressure with a sphygmomanometer. (b) A typical sphygmomanometer uses a valved rubber bulb to inflate the cuff and a diaphragm gauge to measure pressure. (credit a: modification of work by Master Sgt. Jeffrey Allen)

Note:

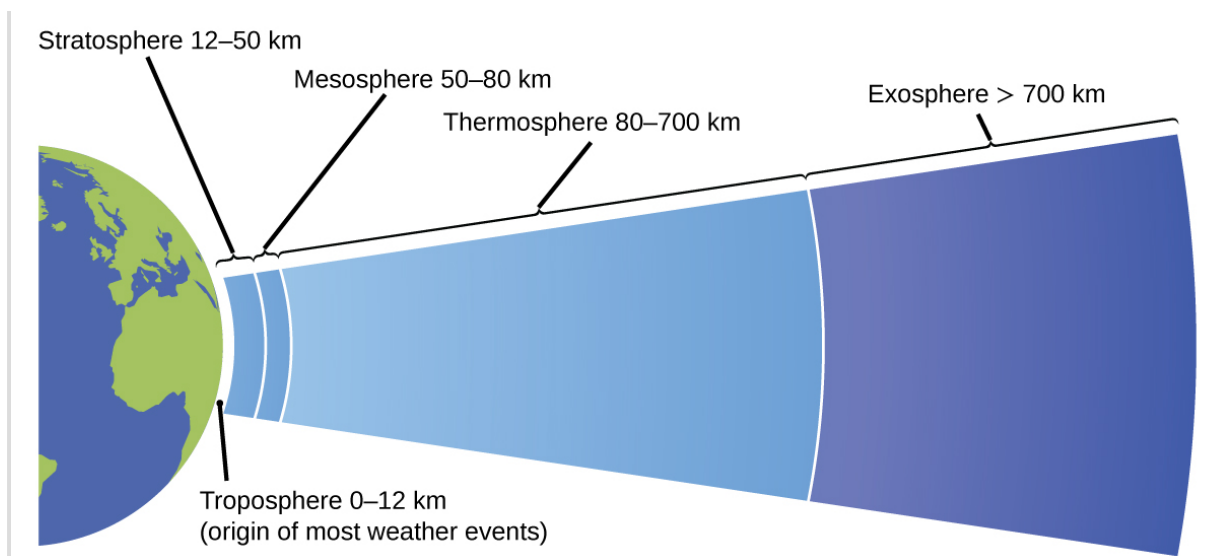
Meteorology, Climatology, and Atmospheric Science

Throughout the ages, people have observed clouds, winds, and precipitation, trying to discern patterns and make predictions: when it is best to plant and harvest; whether it is safe to set out on a sea voyage; and much more. We now face complex weather and atmosphere-related challenges that will have a major impact on our civilization and the ecosystem. Several different scientific disciplines use chemical principles to help us better understand weather, the atmosphere, and climate. These are meteorology, climatology, and atmospheric science. Meteorology is the study of the atmosphere, atmospheric phenomena, and atmospheric effects on earth's weather. Meteorologists seek to understand and predict the weather in the short term, which can save lives and benefit the economy. Weather forecasts ([link](#)) are the result of thousands of measurements of air pressure, temperature, and the like, which are compiled, modeled, and analyzed in weather centers worldwide.



Meteorologists use weather maps to describe and predict weather. Regions of high (H) and low (L) pressure have large effects on weather conditions. The gray lines represent locations of constant pressure known as isobars. (credit: modification of work by National Oceanic and Atmospheric Administration)

In terms of weather, low-pressure systems occur when the earth's surface atmospheric pressure is lower than the surrounding environment: Moist air rises and condenses, producing clouds. Movement of moisture and air within various weather fronts instigates most weather events. The atmosphere is the gaseous layer that surrounds a planet. Earth's atmosphere, which is roughly 100–125 km thick, consists of roughly 78.1% nitrogen and 21.0% oxygen, and can be subdivided further into the regions shown in [\[link\]](#): the exosphere (furthest from earth, > 700 km above sea level), the thermosphere (80–700 km), the mesosphere (50–80 km), the stratosphere (second lowest level of our atmosphere, 12–50 km above sea level), and the troposphere (up to 12 km above sea level, roughly 80% of the earth's atmosphere by mass and the layer where most weather events originate). As you go higher in the troposphere, air density and temperature both decrease.



Earth's atmosphere has five layers: the troposphere, the stratosphere, the mesosphere, the thermosphere, and the exosphere.

Climatology is the study of the climate, averaged weather conditions over long time periods, using atmospheric data. However, climatologists study patterns and effects that occur over decades, centuries, and millennia, rather than shorter time frames of hours, days, and weeks like meteorologists. Atmospheric science is an even broader field, combining meteorology, climatology, and other scientific disciplines that study the atmosphere.

Key Concepts and Summary

Gases exert pressure, which is force per unit area. The pressure of a gas may be expressed in the SI unit of pascal or kilopascal, as well as in many other units including torr, atmosphere, and bar. Atmospheric pressure is measured using a barometer; other gas pressures can be measured using one of several types of manometers.

Key Equations

- $P = \frac{F}{A}$
- $p = h\rho g$

Chemistry End of Chapter Exercises

Exercise:

Problem:

Why are sharp knives more effective than dull knives (Hint: think about the definition of pressure)?

Solution:

The cutting edge of a knife that has been sharpened has a smaller surface area than a dull knife. Since pressure is force per unit area, a sharp knife will exert a higher pressure with the same amount of force and cut through material more effectively.

Exercise:**Problem:**

Why do some small bridges have weight limits that depend on how many wheels or axles the crossing vehicle has?

Exercise:**Problem:**

Why should you roll or belly-crawl rather than walk across a thinly-frozen pond?

Solution:

Lying down distributes your weight over a larger surface area, exerting less pressure on the ice compared to standing up. If you exert less pressure, you are less likely to break through thin ice.

Exercise:**Problem:**

A typical barometric pressure in Redding, California, is about 750 mm Hg. Calculate this pressure in atm and kPa.

Exercise:**Problem:**

A typical barometric pressure in Denver, Colorado, is 615 mm Hg. What is this pressure in atmospheres and kilopascals?

Solution:

0.809 atm; 82.0 kPa

Exercise:

Problem:

A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimeters of mercury, and in kilopascals?

Exercise:**Problem:**

Canadian tire pressure gauges are marked in units of kilopascals. What reading on such a gauge corresponds to 32 psi?

Solution:

$$2.2 \times 10^2 \text{ kPa}$$

Exercise:**Problem:**

During the Viking landings on Mars, the atmospheric pressure was determined to be on the average about 6.50 millibars (1 bar = 0.987 atm). What is that pressure in torr and kPa?

Exercise:**Problem:**

The pressure of the atmosphere on the surface of the planet Venus is about 88.8 atm. Compare that pressure in psi to the normal pressure on earth at sea level in psi.

Solution:

$$\text{Earth: } 14.7 \text{ lb in}^{-2}; \text{ Venus: } 1.31 \times 10^3 \text{ lb in}^{-2}$$

Exercise:**Problem:**

A medical laboratory catalog describes the pressure in a cylinder of a gas as 14.82 MPa. What is the pressure of this gas in atmospheres and torr?

Exercise:**Problem:**

Consider this scenario and answer the following questions: On a mid-August day in the northeastern United States, the following information appeared in the local newspaper: atmospheric pressure at sea level 29.97 in. Hg, 1013.9 mbar.

(a) What was the pressure in kPa?

(b) The pressure near the seacoast in the northeastern United States is usually reported near 30.0 in. Hg. During a hurricane, the pressure may fall to near 28.0 in. Hg. Calculate

the drop in pressure in torr.

Solution:

(a) 101.5 kPa; (b) 51 torr drop

Exercise:

Problem: Why is it necessary to use a nonvolatile liquid in a barometer or manometer?

Exercise:

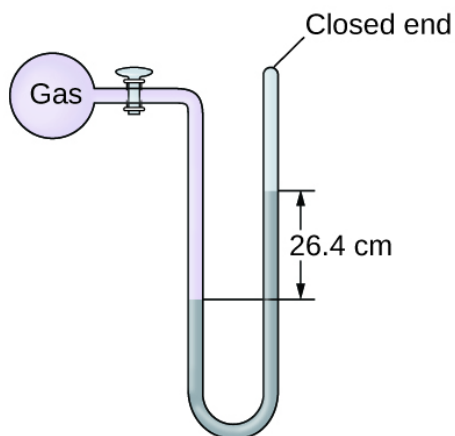
Problem:

The pressure of a sample of gas is measured at sea level with a closed-end manometer. The liquid in the manometer is mercury. Determine the pressure of the gas in:

(a) torr

(b) Pa

(c) bar



Solution:

(a) 264 torr; (b) 35,200 Pa; (c) 0.352 bar

Exercise:

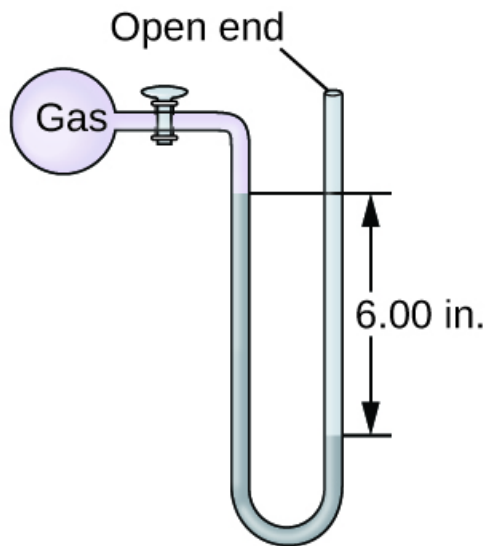
Problem:

The pressure of a sample of gas is measured with an open-end manometer, partially shown to the right. The liquid in the manometer is mercury. Assuming atmospheric pressure is 29.92 in. Hg, determine the pressure of the gas in:

(a) torr

(b) Pa

(c) bar



Exercise:

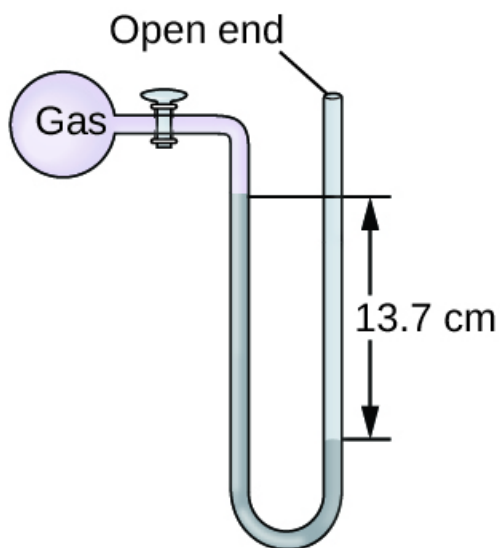
Problem:

The pressure of a sample of gas is measured at sea level with an open-end mercury manometer. Assuming atmospheric pressure is 760.0 mm Hg, determine the pressure of the gas in:

(a) mm Hg

(b) atm

(c) kPa



Solution:

(a) 623 mm Hg; (b) 0.820 atm; (c) 83.1 kPa

Exercise:

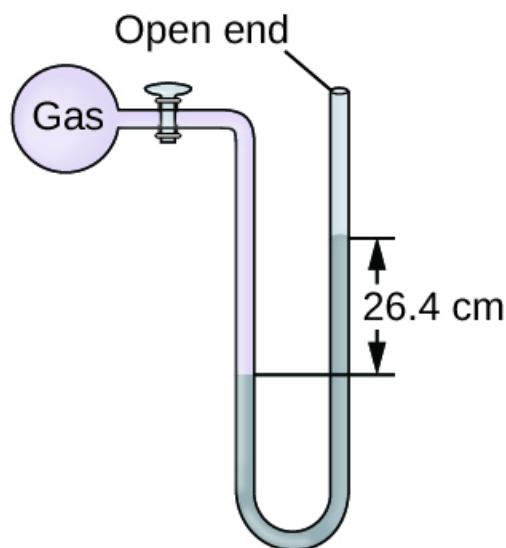
Problem:

The pressure of a sample of gas is measured at sea level with an open-end mercury manometer. Assuming atmospheric pressure is 760 mm Hg, determine the pressure of the gas in:

(a) mm Hg

(b) atm

(c) kPa

**Exercise:****Problem:**

How would the use of a volatile liquid affect the measurement of a gas using open-ended manometers vs. closed-end manometers?

Solution:

With a closed-end manometer, no change would be observed, since the vaporized liquid would contribute equal, opposing pressures in both arms of the manometer tube. However, with an open-ended manometer, a higher pressure reading of the gas would be obtained than expected, since $P_{\text{gas}} = P_{\text{atm}} + P_{\text{vol liquid}}$.

Glossary

atmosphere (atm)

unit of pressure; 1 atm = 101,325 Pa

bar

(bar or b) unit of pressure; 1 bar = 100,000 Pa

barometer

device used to measure atmospheric pressure

hydrostatic pressure

pressure exerted by a fluid due to gravity

manometer

device used to measure the pressure of a gas trapped in a container

pascal (Pa)

SI unit of pressure; $1 \text{ Pa} = 1 \text{ N/m}^2$

pounds per square inch (psi)

unit of pressure common in the US

pressure

force exerted per unit area

torr

unit of pressure; $1 \text{ torr} = \frac{1}{760} \text{ atm}$

The Kinetic-Molecular Theory

- State the postulates of the kinetic-molecular theory
- Use this theory's postulates to explain the gas laws

The gas laws that we have seen to this point, as well as the ideal gas equation, are empirical, that is, they have been derived from experimental observations. The mathematical forms of these laws closely describe the macroscopic behavior of most gases at pressures less than about 1 or 2 atm. Although the gas laws describe relationships that have been verified by many experiments, they do not tell us why gases follow these relationships.

The **kinetic molecular theory** (KMT) is a simple microscopic model that effectively explains the gas laws described in previous modules of this chapter. This theory is based on the following five postulates described here. (Note: The term “molecule” will be used to refer to the individual chemical species that compose the gas, although some gases are composed of atomic species, for example, the noble gases.)

1. Gases are composed of molecules that are in continuous motion, travelling in straight lines and changing direction only when they collide with other molecules or with the walls of a container.
2. The molecules composing the gas are negligibly small compared to the distances between them.
3. The pressure exerted by a gas in a container results from collisions between the gas molecules and the container walls.
4. Gas molecules exert no attractive or repulsive forces on each other or the container walls; therefore, their collisions are *elastic* (do not involve a loss of energy).
5. The average kinetic energy of the gas molecules is proportional to the kelvin temperature of the gas.

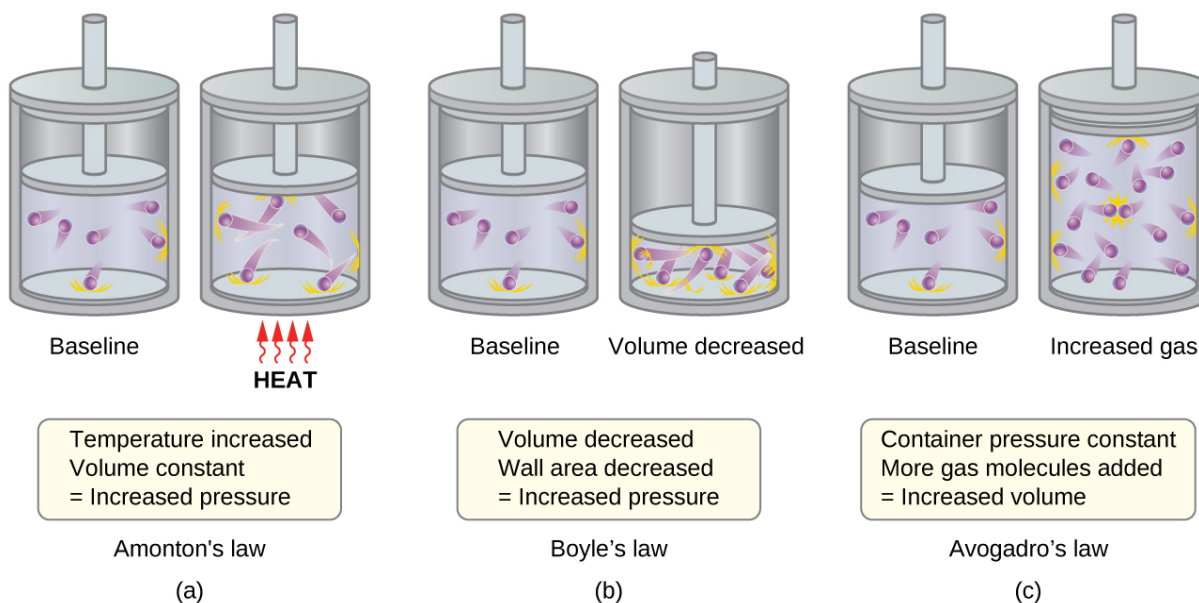
The test of the KMT and its postulates is its ability to explain and describe the behavior of a gas. The various gas laws can be derived from the assumptions of the KMT, which have led chemists to believe that the assumptions of the theory accurately represent the properties of gas molecules. We will first look at the individual gas laws (Boyle's, Charles's, Amontons's, Avogadro's, and Dalton's laws) conceptually to see how the KMT explains them. Then, we will more

carefully consider the relationships between molecular masses, speeds, and kinetic energies with temperature, and explain Graham's law.

The Kinetic-Molecular Theory Explains the Behavior of Gases, Part I

Recalling that gas pressure is exerted by rapidly moving gas molecules and depends directly on the number of molecules hitting a unit area of the wall per unit of time, we see that the KMT conceptually explains the behavior of a gas as follows:

- *Amontons's law.* If the temperature is increased, the average speed and kinetic energy of the gas molecules increase. If the volume is held constant, the increased speed of the gas molecules results in more frequent and more forceful collisions with the walls of the container, therefore increasing the pressure ([\[link\]](#)).
- *Charles's law.* If the temperature of a gas is increased, a constant pressure may be maintained only if the volume occupied by the gas increases. This will result in greater average distances traveled by the molecules to reach the container walls, as well as increased wall surface area. These conditions will decrease the both the frequency of molecule-wall collisions and the number of collisions per unit area, the combined effects of which balance the effect of increased collision forces due to the greater kinetic energy at the higher temperature.
- *Boyle's law.* If the gas volume is decreased, the container wall area decreases and the molecule-wall collision frequency increases, both of which increase the pressure exerted by the gas ([\[link\]](#)).
- *Avogadro's law.* At constant pressure and temperature, the frequency and force of molecule-wall collisions are constant. Under such conditions, increasing the number of gaseous molecules will require a proportional increase in the container volume in order to yield a decrease in the number of collisions per unit area to compensate for the increased frequency of collisions ([\[link\]](#)).
- *Dalton's Law.* Because of the large distances between them, the molecules of one gas in a mixture bombard the container walls with the same frequency whether other gases are present or not, and the total pressure of a gas mixture equals the sum of the (partial) pressures of the individual gases.

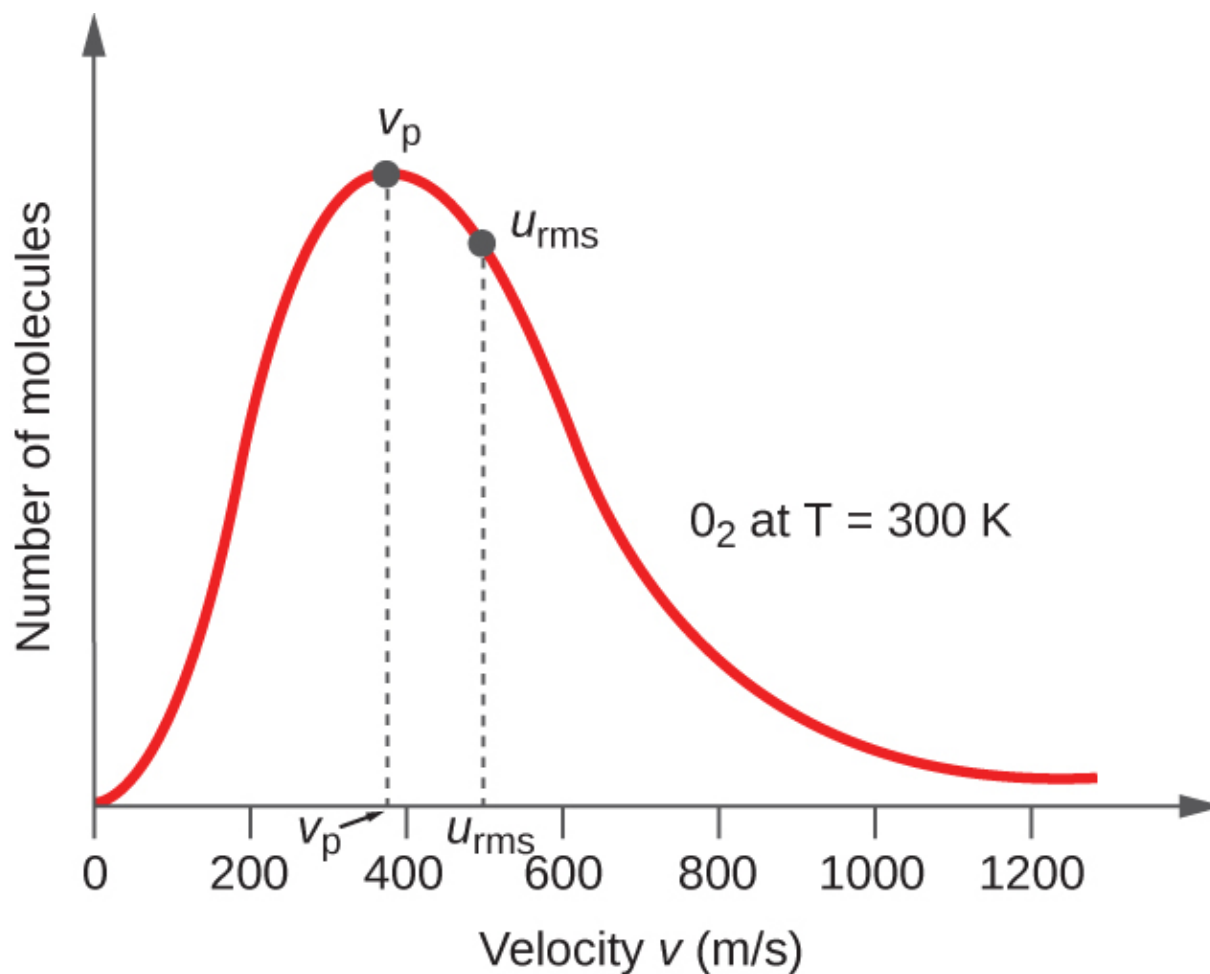


(a) When gas temperature increases, gas pressure increases due to increased force and frequency of molecular collisions. (b) When volume decreases, gas pressure increases due to increased frequency of molecular collisions. (c) When the amount of gas increases at a constant pressure, volume increases to yield a constant number of collisions per unit wall area per unit time.

Molecular Velocities and Kinetic Energy

The previous discussion showed that the KMT qualitatively explains the behaviors described by the various gas laws. The postulates of this theory may be applied in a more quantitative fashion to derive these individual laws. To do this, we must first look at velocities and kinetic energies of gas molecules, and the temperature of a gas sample.

In a gas sample, individual molecules have widely varying speeds; however, because of the *vast* number of molecules and collisions involved, the molecular speed distribution and average speed are constant. This molecular speed distribution is known as a Maxwell-Boltzmann distribution, and it depicts the relative numbers of molecules in a bulk sample of gas that possesses a given speed ([link](#)).



The molecular speed distribution for oxygen gas at 300 K is shown here.

Very few molecules move at either very low or very high speeds. The number of molecules with intermediate speeds increases rapidly up to a maximum, which is the most probable speed, then drops off rapidly. Note that the most probable speed, v_p , is a little less than 400 m/s, while the root mean square speed, u_{rms} , is closer to 500 m/s.

The kinetic energy (KE) of a particle of mass (m) and speed (u) is given by:

Equation:

$$KE = \frac{1}{2} mu^2$$

Expressing mass in kilograms and speed in meters per second will yield energy values in units of joules ($J = \text{kg m}^2 \text{s}^{-2}$). To deal with a large number of gas molecules, we use averages for both speed and kinetic energy. In the KMT, the **root mean square velocity** of a particle, u_{rms} , is defined as the square root of the average of the squares of the velocities with n = the number of particles:

Equation:

$$u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \dots}{n}}$$

The average kinetic energy for a mole of particles, KE_{avg} , is then equal to:

Equation:

$$\text{KE}_{\text{avg}} = \frac{1}{2} M u_{\text{rms}}^2$$

The KE_{avg} of a mole of gas molecules is also directly proportional to the temperature of the gas and may be described by the equation:

Equation:

$$\text{KE}_{\text{avg}} = \frac{3}{2} RT$$

where R is the gas constant and T is the kelvin temperature. When used in this equation, the appropriate form of the gas constant is $8.314 \text{ J/mol}\cdot\text{K}$ ($8.314 \text{ kg m}^2\text{s}^{-2}\text{mol}^{-1}\text{K}^{-1}$). These two separate equations for KE_{avg} may be combined and rearranged to yield a relation between molecular speed and temperature:

Equation:

$$\frac{1}{2} M u_{\text{rms}}^2 = \frac{3}{2} RT$$

Equation:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

Example:**Calculation of u_{rms}**

Calculate the root-mean-square velocity for a nitrogen molecule at 30 °C.

Solution

Convert the temperature into Kelvin:

Equation:

$$30\text{ }^{\circ}\text{C} + 273 = 303\text{ K}$$

Determine the molar mass of nitrogen in kilograms:

Equation:

$$\frac{28.0\text{ g}}{1\text{ mol}} \times \frac{1\text{ kg}}{1000\text{ g}} = 0.028\text{ kg/mol}$$

Replace the variables and constants in the root-mean-square velocity equation, replacing Joules with the equivalent $\text{kg m}^2\text{s}^{-2}$:

Equation:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{m}}$$

Equation:

$$u_{\text{rms}} = \sqrt{\frac{3(8.314\text{ J/mol K})(303\text{ K})}{(0.028\text{ kg/mol})}} = \sqrt{2.70 \times 10^5\text{ m}^2\text{s}^{-2}} = 519\text{ m/s}$$

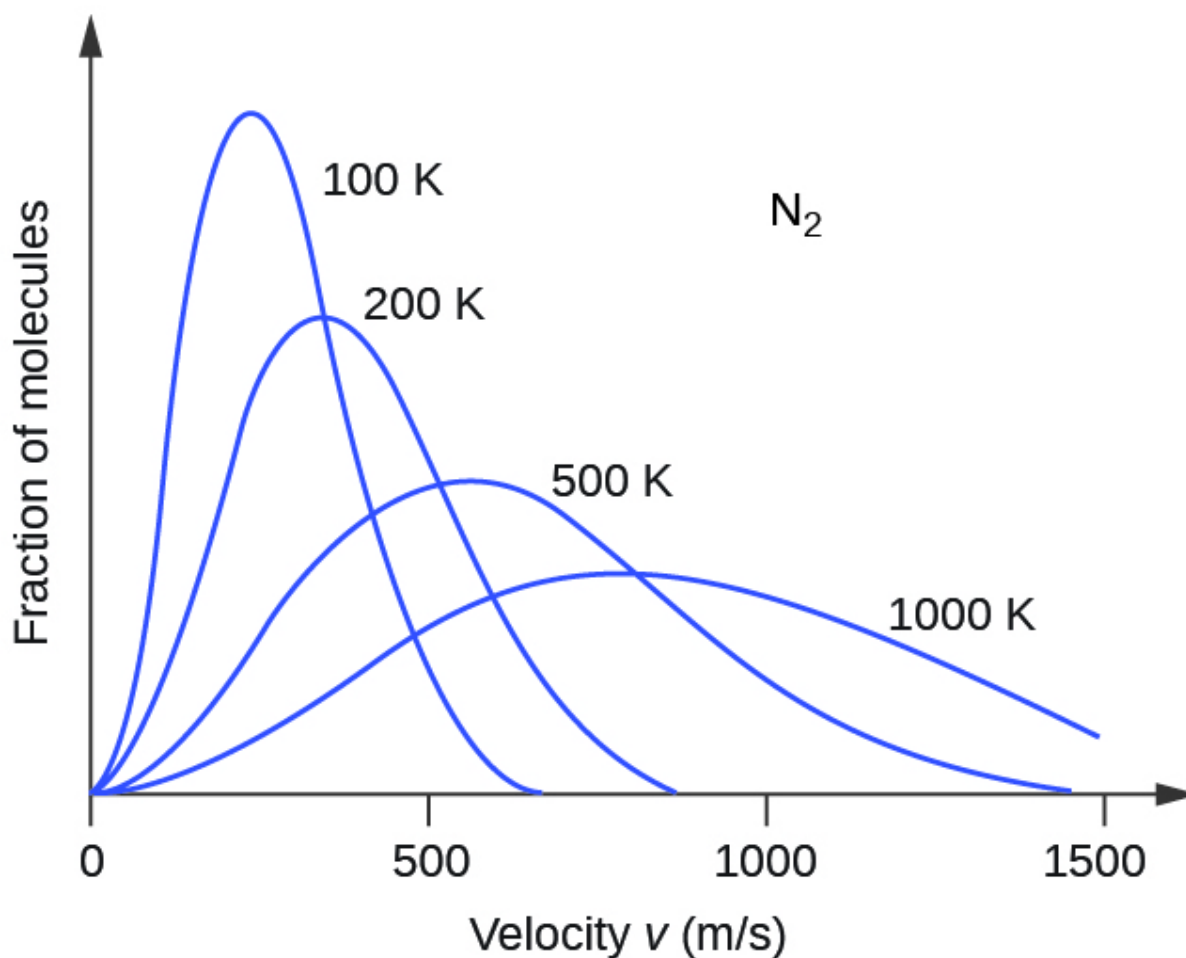
Check Your Learning

Calculate the root-mean-square velocity for a mole of oxygen molecules at – 23 °C.

Note:**Answer:**

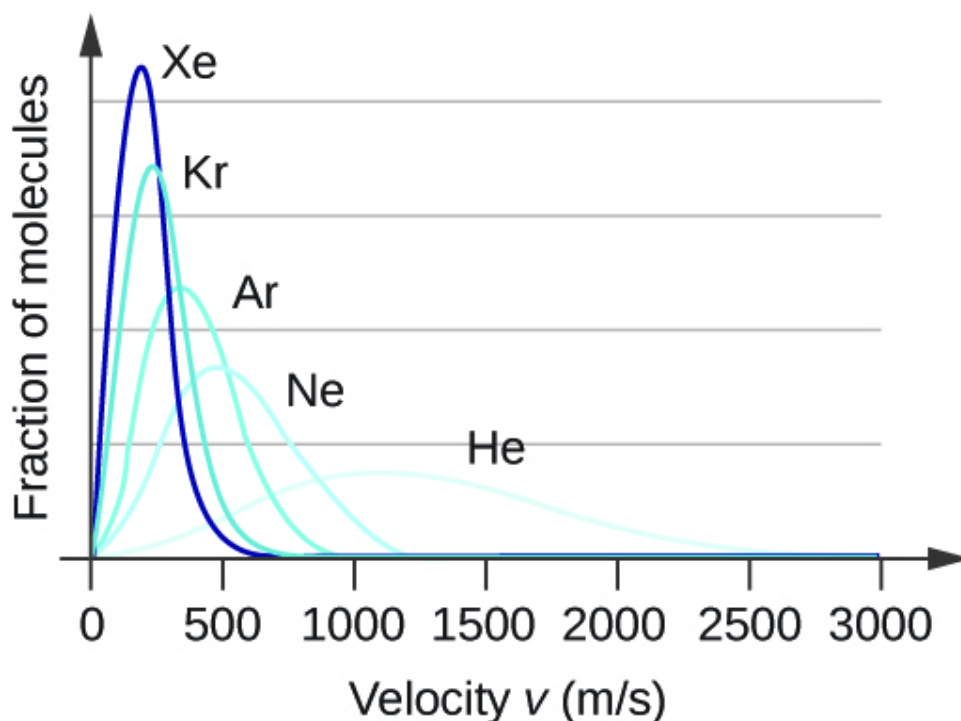
441 m/s

If the temperature of a gas increases, its KE_{avg} increases, more molecules have higher speeds and fewer molecules have lower speeds, and the distribution shifts toward higher speeds overall, that is, to the right. If temperature decreases, KE_{avg} decreases, more molecules have lower speeds and fewer molecules have higher speeds, and the distribution shifts toward lower speeds overall, that is, to the left. This behavior is illustrated for nitrogen gas in [\[link\]](#).



The molecular speed distribution for nitrogen gas (N_2) shifts to the right and flattens as the temperature increases; it shifts to the left and heightens as the temperature decreases.

At a given temperature, all gases have the same KE_{avg} for their molecules. Gases composed of lighter molecules have more high-speed particles and a higher u_{rms} , with a speed distribution that peaks at relatively higher velocities. Gases consisting of heavier molecules have more low-speed particles, a lower u_{rms} , and a speed distribution that peaks at relatively lower velocities. This trend is demonstrated by the data for a series of noble gases shown in [\[link\]](#).



Molecular velocity is directly related to molecular mass. At a given temperature, lighter molecules move faster on average than heavier molecules.

Note:



The [gas simulator](#) may be used to examine the effect of temperature on molecular velocities. Examine the simulator's "energy histograms" (molecular speed distributions) and "species information" (which gives average speed values) for molecules of different masses at various temperatures.

The Kinetic-Molecular Theory Explains the Behavior of Gases, Part II

According to Graham's law, the molecules of a gas are in rapid motion and the molecules themselves are small. The average distance between the molecules of a gas is large compared to the size of the molecules. As a consequence, gas molecules can move past each other easily and diffuse at relatively fast rates.

The rate of effusion of a gas depends directly on the (average) speed of its molecules:

Equation:

$$\text{effusion rate} \propto u_{\text{rms}}$$

Using this relation, and the equation relating molecular speed to mass, Graham's law may be easily derived as shown here:

Equation:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

Equation:

$$M = \frac{3RT}{u_{\text{rms}}^2} = \frac{3RT}{\bar{u}^2}$$

Equation:

$$\frac{\text{effusion rate A}}{\text{effusion rate B}} = \frac{u_{\text{rms A}}}{u_{\text{rms B}}} = \frac{\sqrt{\frac{3RT}{M_{\text{A}}}}}{\sqrt{\frac{3RT}{M_{\text{B}}}}} = \sqrt{\frac{M_{\text{B}}}{M_{\text{A}}}}$$

The ratio of the rates of effusion is thus derived to be inversely proportional to the ratio of the square roots of their masses. This is the same relation observed experimentally and expressed as Graham's law.

Key Concepts and Summary

The kinetic molecular theory is a simple but very effective model that effectively explains ideal gas behavior. The theory assumes that gases consist of widely separated molecules of negligible volume that are in constant motion, colliding elastically with one another and the walls of their container with average velocities determined by their absolute temperatures. The individual molecules of a gas exhibit a range of velocities, the distribution of these velocities being dependent on the temperature of the gas and the mass of its molecules.

Key Equations

- $u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \dots}{n}}$
- $\text{KE}_{\text{avg}} = \frac{3}{2}RT$
- $u_{\text{rms}} = \sqrt{\frac{3RT}{m}}$

Chemistry End of Chapter Exercises

Exercise:

Problem:

Using the postulates of the kinetic molecular theory, explain why a gas uniformly fills a container of any shape.

Exercise:**Problem:**

Can the speed of a given molecule in a gas double at constant temperature? Explain your answer.

Solution:

Yes. At any given instant, there are a range of values of molecular speeds in a sample of gas. Any single molecule can speed up or slow down as it collides with other molecules. The average velocity of all the molecules is constant at constant temperature.

Exercise:**Problem:**

Describe what happens to the average kinetic energy of ideal gas molecules when the conditions are changed as follows:

- (a) The pressure of the gas is increased by reducing the volume at constant temperature.
- (b) The pressure of the gas is increased by increasing the temperature at constant volume.
- (c) The average velocity of the molecules is increased by a factor of 2.

Exercise:**Problem:**

The distribution of molecular velocities in a sample of helium is shown in [\[link\]](#). If the sample is cooled, will the distribution of velocities look more like that of H_2 or of H_2O ? Explain your answer.

Solution:

H₂O. Cooling slows the velocities of the He atoms, causing them to behave as though they were heavier.

Exercise:

Problem:

What is the ratio of the average kinetic energy of a SO₂ molecule to that of an O₂ molecule in a mixture of two gases? What is the ratio of the root mean square speeds, u_{rms} , of the two gases?

Exercise:

Problem:

A 1-L sample of CO initially at STP is heated to 546 K, and its volume is increased to 2 L.

- (a) What effect do these changes have on the number of collisions of the molecules of the gas per unit area of the container wall?
- (b) What is the effect on the average kinetic energy of the molecules?
- (c) What is the effect on the root mean square speed of the molecules?

Solution:

- (a) The number of collisions per unit area of the container wall is constant.
- (b) The average kinetic energy doubles. (c) The root mean square speed increases to $\sqrt{2}$ times its initial value; u_{rms} is proportional to $\sqrt{\text{KE}_{\text{avg}}}$.

Exercise:

Problem:

The root mean square speed of H₂ molecules at 25 °C is about 1.6 km/s. What is the root mean square speed of a N₂ molecule at 25 °C?

Exercise:

Problem: Answer the following questions:

- (a) Is the pressure of the gas in the hot air balloon shown at the opening of this chapter greater than, less than, or equal to that of the atmosphere outside the balloon?
- (b) Is the density of the gas in the hot air balloon shown at the opening of this chapter greater than, less than, or equal to that of the atmosphere outside the balloon?
- (c) At a pressure of 1 atm and a temperature of 20 °C, dry air has a density of 1.2256 g/L. What is the (average) molar mass of dry air?
- (d) The average temperature of the gas in a hot air balloon is 1.30×10^2 °F. Calculate its density, assuming the molar mass equals that of dry air.
- (e) The lifting capacity of a hot air balloon is equal to the difference in the mass of the cool air displaced by the balloon and the mass of the gas in the balloon. What is the difference in the mass of 1.00 L of the cool air in part (c) and the hot air in part (d)?
- (f) An average balloon has a diameter of 60 feet and a volume of 1.1×10^5 ft³. What is the lifting power of such a balloon? If the weight of the balloon and its rigging is 500 pounds, what is its capacity for carrying passengers and cargo?
- (g) A balloon carries 40.0 gallons of liquid propane (density 0.5005 g/L). What volume of CO₂ and H₂O gas is produced by the combustion of this propane?
- (h) A balloon flight can last about 90 minutes. If all of the fuel is burned during this time, what is the approximate rate of heat loss (in kJ/min) from the hot air in the bag during the flight?
-

Solution:

- (a) equal; (b) less than; (c) 29.48 g mol⁻¹; (d) 1.0966 g L⁻¹; (e) 0.129 g/L; (f) 4.01×10^5 g; net lifting capacity = 384 lb; (g) 270 L; (h) 39.1 kJ min⁻¹

Exercise:

Problem:

Show that the ratio of the rate of diffusion of Gas 1 to the rate of diffusion of Gas 2, $\frac{R_1}{R_2}$, is the same at 0 °C and 100 °C.

Glossary

kinetic molecular theory

theory based on simple principles and assumptions that effectively explains ideal gas behavior

root mean square velocity (u_{rms})

measure of average velocity for a group of particles calculated as the square root of the average squared velocity

Non-Ideal Gas Behavior

By the end of this section, you will be able to:

- Describe the physical factors that lead to deviations from ideal gas behavior
- Explain how these factors are represented in the van der Waals equation
- Define compressibility (Z) and describe how its variation with pressure reflects non-ideal behavior
- Quantify non-ideal behavior by comparing computations of gas properties using the ideal gas law and the van der Waals equation

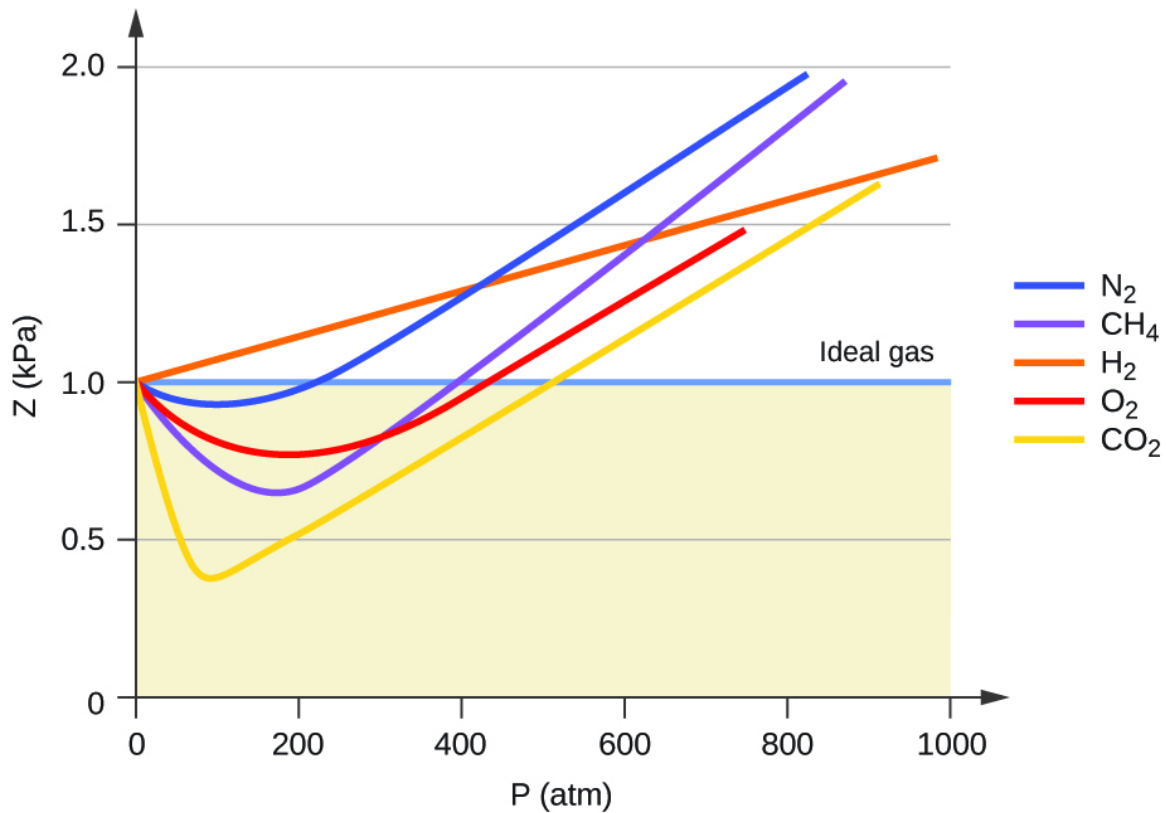
Thus far, the ideal gas law, $PV = nRT$, has been applied to a variety of different types of problems, ranging from reaction stoichiometry and empirical and molecular formula problems to determining the density and molar mass of a gas. As mentioned in the previous modules of this chapter, however, the behavior of a gas is often non-ideal, meaning that the observed relationships between its pressure, volume, and temperature are not accurately described by the gas laws. In this section, the reasons for these deviations from ideal gas behavior are considered.

One way in which the accuracy of $PV = nRT$ can be judged is by comparing the actual volume of 1 mole of gas (its molar volume, V_m) to the molar volume of an ideal gas at the same temperature and pressure. This ratio is called the **compressibility factor (Z)** with:

Equation:

$$Z = \frac{\text{molar volume of gas at same } T \text{ and } P}{\text{molar volume of ideal gas at same } T \text{ and } P} = \left(\frac{PV_m}{RT} \right)_{\text{measured}}$$

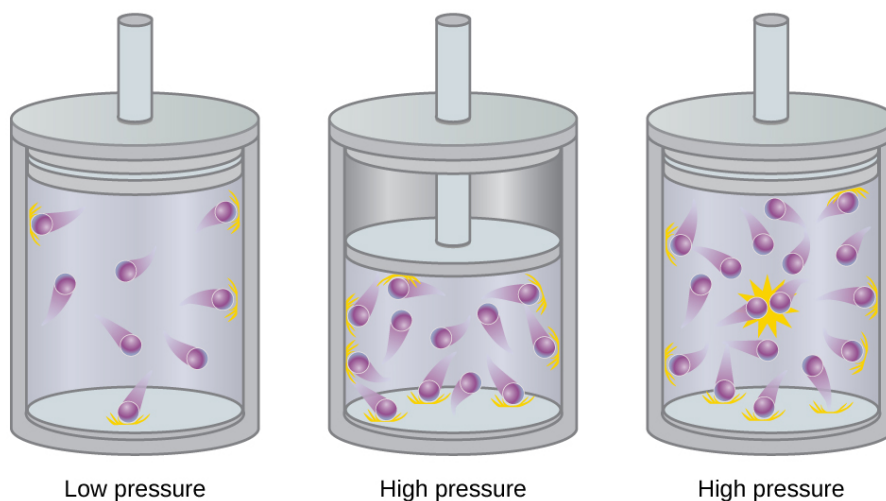
Ideal gas behavior is therefore indicated when this ratio is equal to 1, and any deviation from 1 is an indication of non-ideal behavior. [\[link\]](#) shows plots of Z over a large pressure range for several common gases.



A graph of the compressibility factor (Z) vs. pressure shows that gases can exhibit significant deviations from the behavior predicted by the ideal gas law.

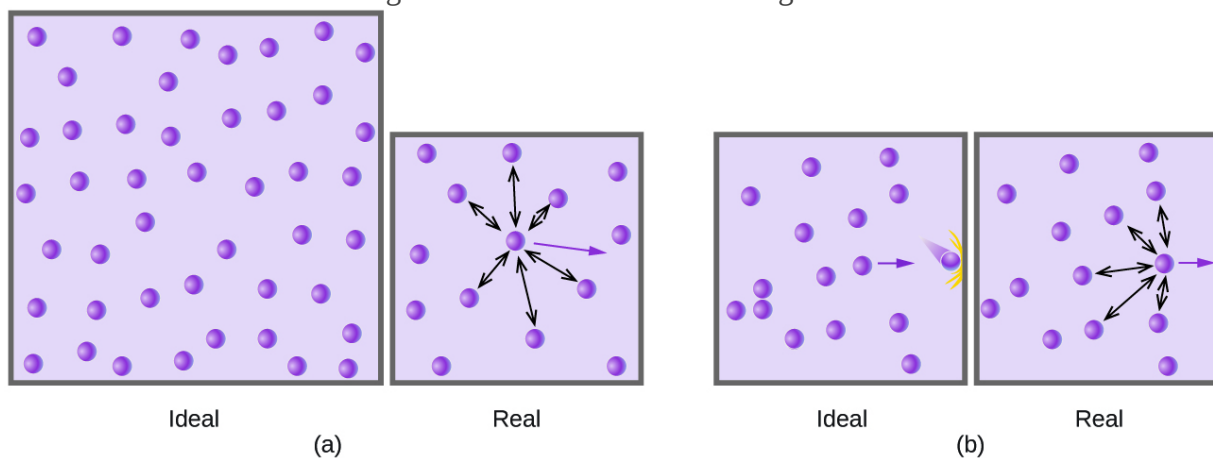
As is apparent from [\[link\]](#), the ideal gas law does not describe gas behavior well at relatively high pressures. To determine why this is, consider the differences between real gas properties and what is expected of a hypothetical ideal gas.

Particles of a hypothetical ideal gas have no significant volume and do not attract or repel each other. In general, real gases approximate this behavior at relatively low pressures and high temperatures. However, at high pressures, the molecules of a gas are crowded closer together, and the amount of empty space between the molecules is reduced. At these higher pressures, the volume of the gas molecules themselves becomes appreciable relative to the total volume occupied by the gas ([\[link\]](#)). The gas therefore becomes less compressible at these high pressures, and although its volume continues to decrease with increasing pressure, this decrease is not *proportional* as predicted by Boyle's law.



Raising the pressure of a gas increases the fraction of its volume that is occupied by the gas molecules and makes the gas less compressible.

At relatively low pressures, gas molecules have practically no attraction for one another because they are (on average) so far apart, and they behave almost like particles of an ideal gas. At higher pressures, however, the force of attraction is also no longer insignificant. This force pulls the molecules a little closer together, slightly decreasing the pressure (if the volume is constant) or decreasing the volume (at constant pressure) ([link](#)). This change is more pronounced at low temperatures because the molecules have lower KE relative to the attractive forces, and so they are less effective in overcoming these attractions after colliding with one another.



- (a) Attractions between gas molecules serve to decrease the gas volume at constant pressure compared to an ideal gas whose molecules experience no attractive forces. (b) These attractive forces will decrease the force of collisions between the molecules and container walls, therefore reducing the pressure exerted compared to an ideal gas.

There are several different equations that better approximate gas behavior than does the ideal gas law. The first, and simplest, of these was developed by the Dutch scientist Johannes van der Waals in 1879. The **van der Waals equation** improves upon the ideal gas law by adding two terms: one to account for the volume of the gas molecules and another for the attractive forces between them.

$$PV = nRT \longrightarrow \left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

Correction for molecular attraction
Correction for volume of molecules

The constant a corresponds to the strength of the attraction between molecules of a particular gas, and the constant b corresponds to the size of the molecules of a particular gas. The “correction” to the pressure term in the ideal gas law is $\frac{n^2a}{V^2}$, and the “correction” to the volume is nb . Note that when V is relatively large and n is relatively small, both of these correction terms become negligible, and the van der Waals equation reduces to the ideal gas law, $PV = nRT$. Such a condition corresponds to a gas in which a relatively low number of molecules is occupying a relatively large volume, that is, a gas at a relatively low pressure. Experimental values for the van der Waals constants of some common gases are given in [\[link\]](#).

Values of van der Waals Constants for Some Common Gases		
Gas	a (L ² atm/mol ²)	b (L/mol)
N ₂	1.39	0.0391
O ₂	1.36	0.0318
CO ₂	3.59	0.0427
H ₂ O	5.46	0.0305
He	0.0342	0.0237
CCl ₄	20.4	0.1383

At low pressures, the correction for intermolecular attraction, a , is more important than the one for molecular volume, b . At high pressures and small volumes, the correction for the volume of the molecules becomes important because the molecules themselves are incompressible and constitute an appreciable fraction of the total volume. At some intermediate pressure, the two corrections have opposing influences and the gas appears to follow the relationship given by $PV =$

nRT over a small range of pressures. This behavior is reflected by the “dips” in several of the compressibility curves shown in [\[link\]](#). The attractive force between molecules initially makes the gas more compressible than an ideal gas, as pressure is raised (Z decreases with increasing P). At very high pressures, the gas becomes less compressible (Z increases with P), as the gas molecules begin to occupy an increasingly significant fraction of the total gas volume.

Strictly speaking, the ideal gas equation functions well when intermolecular attractions between gas molecules are negligible and the gas molecules themselves do not occupy an appreciable part of the whole volume. These criteria are satisfied under conditions of *low pressure and high temperature*. Under such conditions, the gas is said to behave ideally, and deviations from the gas laws are small enough that they may be disregarded—this is, however, very often not the case.

Example:

Comparison of Ideal Gas Law and van der Waals Equation

A 4.25-L flask contains 3.46 mol CO_2 at 229 °C. Calculate the pressure of this sample of CO_2 :

- from the ideal gas law
- from the van der Waals equation
- Explain the reason(s) for the difference.

Solution

- From the ideal gas law:

Equation:

$$P = \frac{nRT}{V} = \frac{3.46 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 502 \text{ K}}{4.25 \text{ L}} = 33.5 \text{ atm}$$

- From the van der Waals equation:

Equation:

$$\left(P + \frac{n^2a}{V^2}\right) \times (V - nb) = nRT \longrightarrow P = \frac{nRT}{(V - nb)} - \frac{n^2a}{V^2}$$

Equation:

$$P = \frac{3.46 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 502 \text{ K}}{(4.25 \text{ L} - 3.46 \text{ mol} \times 0.0427 \text{ L mol}^{-1})} - \frac{(3.46 \text{ mol})^2 \times 3.59 \text{ L}^2 \text{ atm mol}^{-2}}{(4.25 \text{ L})^2}$$

This finally yields $P = 32.4 \text{ atm}$.

- This is not very different from the value from the ideal gas law because the pressure is not very high and the temperature is not very low. The value is somewhat different because CO_2 molecules do have some volume and attractions between molecules, and the ideal gas law assumes they do not have volume or attractions.

Check your Learning

A 560-mL flask contains 21.3 g N_2 at 145 °C. Calculate the pressure of N_2 :

- from the ideal gas law
- from the van der Waals equation
- Explain the reason(s) for the difference.

Note:**Answer:**

(a) 46.562 atm; (b) 46.594 atm; (c) The van der Waals equation takes into account the volume of the gas molecules themselves as well as intermolecular attractions.

Key Concepts and Summary

Gas molecules possess a finite volume and experience forces of attraction for one another. Consequently, gas behavior is not necessarily described well by the ideal gas law. Under conditions of low pressure and high temperature, these factors are negligible, the ideal gas equation is an accurate description of gas behavior, and the gas is said to exhibit ideal behavior. However, at lower temperatures and higher pressures, corrections for molecular volume and molecular attractions are required to account for finite molecular size and attractive forces. The van der Waals equation is a modified version of the ideal gas law that can be used to account for the non-ideal behavior of gases under these conditions.

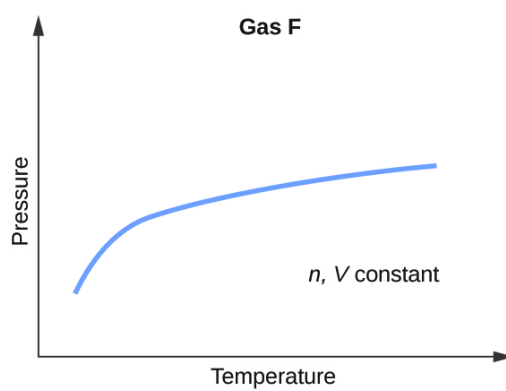
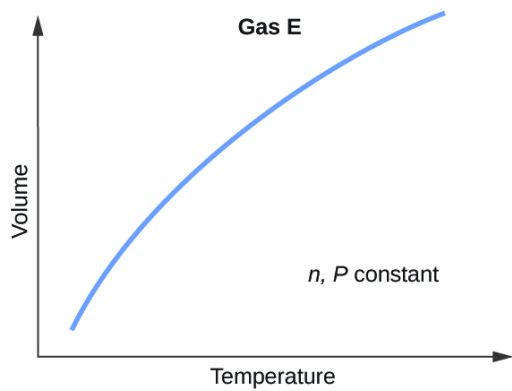
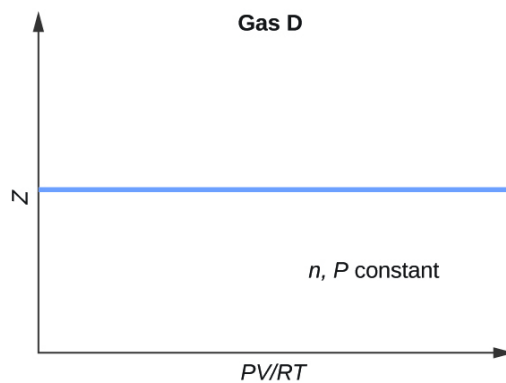
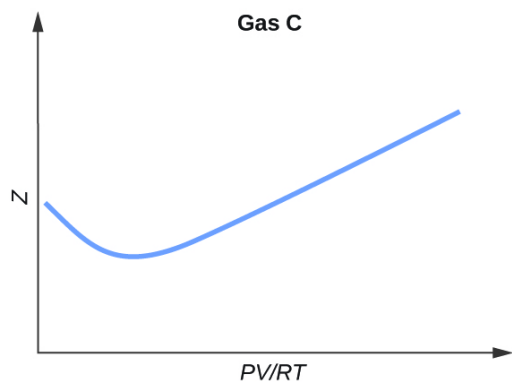
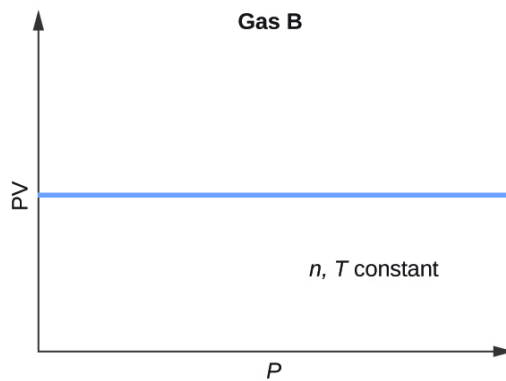
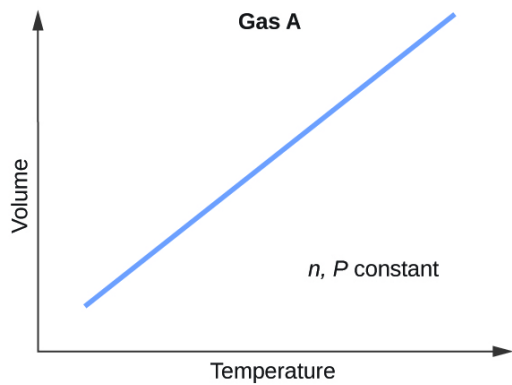
Key Equations

- $$Z = \frac{\text{molar volume of gas at same } T \text{ and } P}{\text{molar volume of ideal gas at same } T \text{ and } P} = \left(\frac{P \times V_m}{R \times T} \right)_{\text{measured}}$$
- $$\left(P + \frac{n^2 a}{V^2} \right) \times (V - nb) = nRT$$

Chemistry End of Chapter Exercises

Exercise:**Problem:**

Graphs showing the behavior of several different gases follow. Which of these gases exhibit behavior significantly different from that expected for ideal gases?

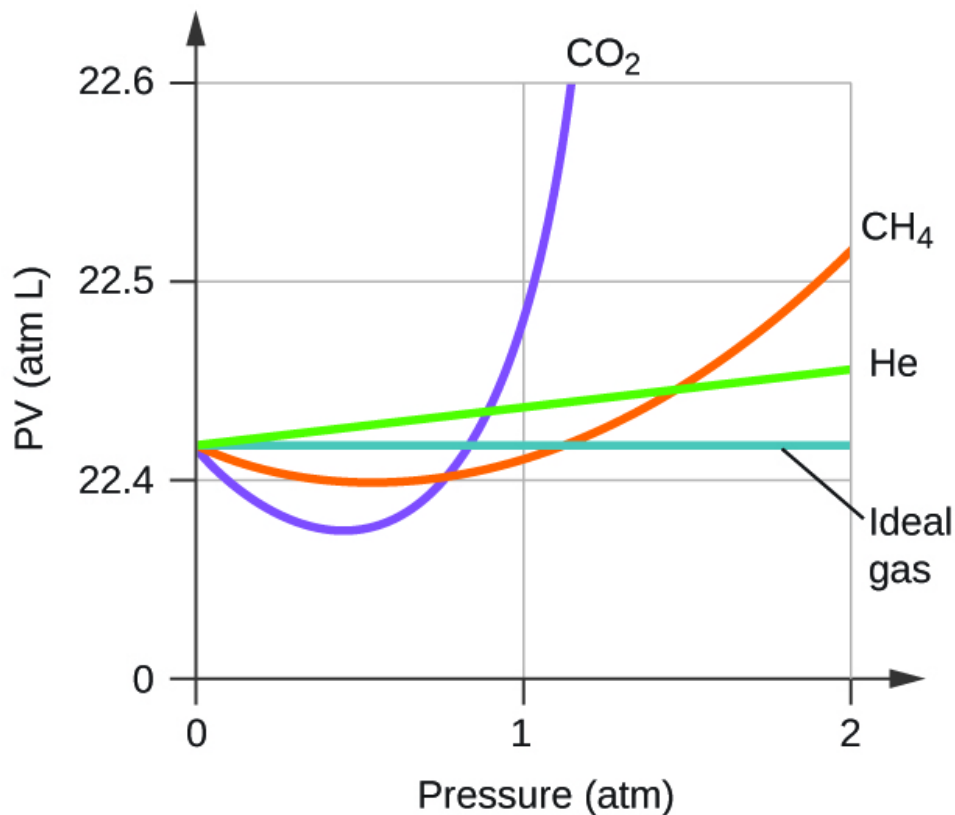


Solution:

Gases C, E, and F

Exercise:

Problem: Explain why the plot of PV for CO_2 differs from that of an ideal gas.



Exercise:

Problem:

Under which of the following sets of conditions does a real gas behave most like an ideal gas, and for which conditions is a real gas expected to deviate from ideal behavior? Explain.

- (a) high pressure, small volume
- (b) high temperature, low pressure
- (c) low temperature, high pressure

Solution:

The gas behavior most like an ideal gas will occur under the conditions in (b). Molecules have high speeds and move through greater distances between collision; they also have shorter contact times and interactions are less likely. Deviations occur with the conditions described in (a) and (c). Under conditions of (a), some gases may liquefy. Under conditions of (c), most gases will liquefy.

Exercise:

Problem:

Describe the factors responsible for the deviation of the behavior of real gases from that of an ideal gas.

Exercise:**Problem:**

For which of the following gases should the correction for the molecular volume be largest: CO, CO₂, H₂, He, NH₃, SF₆?

Solution:

SF₆

Exercise:

Problem: A 0.245-L flask contains 0.467 mol CO₂ at 159 °C. Calculate the pressure:

- (a) using the ideal gas law
- (b) using the van der Waals equation
- (c) Explain the reason for the difference.
- (d) Identify which correction (that for P or V) is dominant and why.

Exercise:

Problem: Answer the following questions:

- (a) If XX behaved as an ideal gas, what would its graph of Z vs. P look like?
- (b) For most of this chapter, we performed calculations treating gases as ideal. Was this justified?
- (c) What is the effect of the volume of gas molecules on Z? Under what conditions is this effect small? When is it large? Explain using an appropriate diagram.
- (d) What is the effect of intermolecular attractions on the value of Z? Under what conditions is this effect small? When is it large? Explain using an appropriate diagram.
- (e) In general, under what temperature conditions would you expect Z to have the largest deviations from the Z for an ideal gas?

Solution:

(a) A straight horizontal line at 1.0; (b) When real gases are at low pressures and high temperatures they behave close enough to ideal gases that they are approximated as such, however, in some cases, we see that at a high pressure and temperature, the ideal gas approximation breaks down and is significantly different from the pressure calculated by the ideal gas equation (c) The greater the compressibility, the more the volume matters. At low pressures, the correction factor for intermolecular attractions is more significant, and the effect of the volume of the gas molecules on Z would be a small lowering compressibility. At higher pressures, the effect of the volume of the gas molecules themselves on Z would increase compressibility (see [\[link\]](#)) (d) Once again, at low pressures, the effect of intermolecular attractions on Z would be more important than the correction factor for the volume of the gas molecules themselves, though perhaps still small. At higher pressures and low temperatures, the effect of intermolecular attractions would be larger. See [\[link\]](#). (e) low temperatures

Glossary

compressibility factor (Z)

ratio of the experimentally measured molar volume for a gas to its molar volume as computed from the ideal gas equation

van der Waals equation

modified version of the ideal gas equation containing additional terms to account for non-ideal gas behavior

Introduction

class="introduction"

- Intermolecular Forces
- Properties of Liquids
- Phase Transitions
- Phase Diagrams
- The Solid State of Matter
- Lattice Structures in Crystalline Solids

Solid carbon
dioxide

("dry ice",
left)

sublimes
vigorously
when placed
in a liquid
(right),
cooling the
liquid and
generating a
fog of
condensed
water vapor
above the
cylinder.
(credit:
modificatio
n of work
by Paul
Flowers)



The great distances between atoms and molecules in a gaseous phase, and the corresponding absence of any significant interactions between them, allows for simple descriptions of many physical properties that are the same for all gases, regardless of their chemical identities. As described in the final module of the chapter on gases, this situation changes at high pressures and low temperatures—conditions that permit the atoms and molecules to interact to a much greater extent. In the liquid and solid states, these interactions are of considerable strength and play an important role in determining a number of physical properties that *do* depend on the chemical identity of the substance. In this chapter, the nature of these interactions and their effects on various physical properties of liquid and solid phases will be examined.

Intermolecular Forces

By the end of this section, you will be able to:

- Describe the types of intermolecular forces possible between atoms or molecules in condensed phases (dispersion forces, dipole-dipole attractions, and hydrogen bonding)
- Identify the types of intermolecular forces experienced by specific molecules based on their structures
- Explain the relation between the intermolecular forces present within a substance and the temperatures associated with changes in its physical state

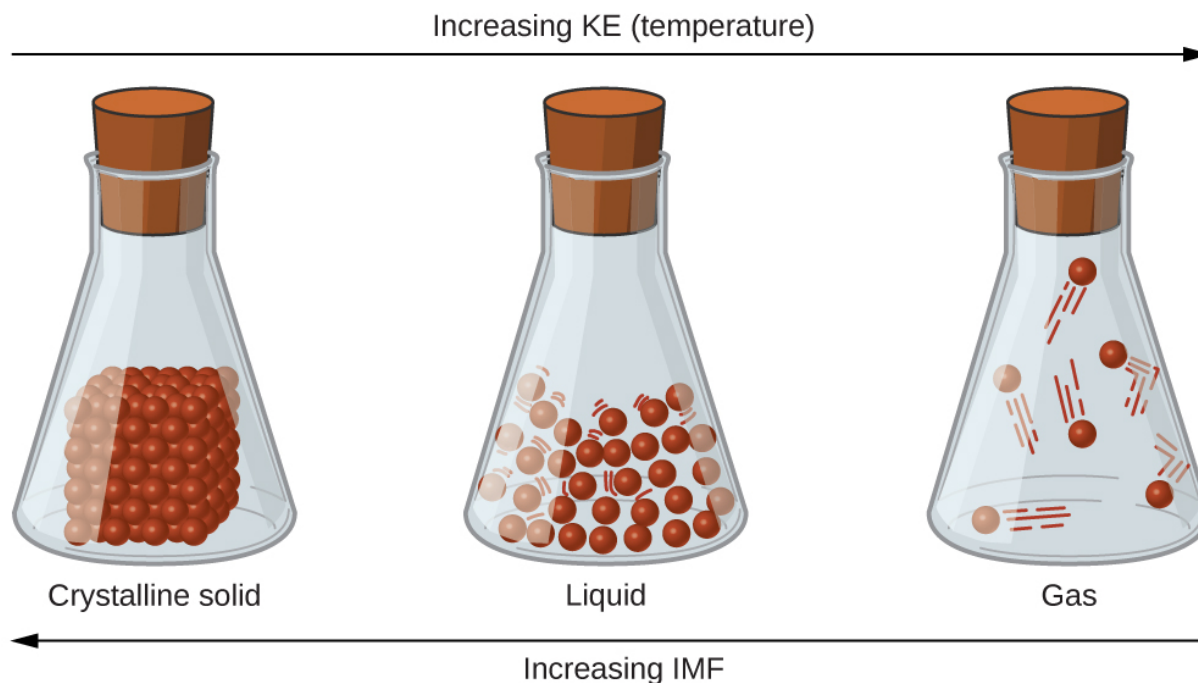
As was the case for gaseous substances, the kinetic molecular theory may be used to explain the behavior of solids and liquids. In the following description, the term *particle* will be used to refer to an atom, molecule, or ion. Note that we will use the popular phrase “intermolecular attraction” to refer to attractive forces between the particles of a substance, regardless of whether these particles are molecules, atoms, or ions.

Consider these two aspects of the molecular-level environments in solid, liquid, and gaseous matter:

- Particles in a solid are tightly packed together and often arranged in a regular pattern; in a liquid, they are close together with no regular arrangement; in a gas, they are far apart with no regular arrangement.
- Particles in a solid vibrate about fixed positions and do not generally move in relation to one another; in a liquid, they move past each other but remain in essentially constant contact; in a gas, they move independently of one another except when they collide.

The differences in the properties of a solid, liquid, or gas reflect the strengths of the attractive forces between the atoms, molecules, or ions that make up each phase. The phase in which a substance exists depends on the relative extents of its **intermolecular forces** (IMFs) and the kinetic energies (KE) of its molecules. IMFs are the various forces of attraction that may exist between the atoms and molecules of a substance due to electrostatic phenomena, as will be detailed in this module. These forces serve to hold particles close together, whereas the particles' KE provides the energy

required to overcome the attractive forces and thus increase the distance between particles. [\[link\]](#) illustrates how changes in physical state may be induced by changing the temperature, hence, the average KE, of a given substance.



Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.)

As an example of the processes depicted in this figure, consider a sample of water. When gaseous water is cooled sufficiently, the attractions between H_2O molecules will be capable of holding them together when they come into contact with each other; the gas condenses, forming liquid H_2O . For example, liquid water forms on the outside of a cold glass as the water vapor in the air is cooled by the cold glass, as seen in [\[link\]](#).



(a)



(b)

Condensation forms when water vapor in the air is cooled enough to form liquid water, such as (a) on the outside of a cold beverage glass or (b) in the form of fog. (credit a: modification of work by Jenny Downing; credit b: modification of work by Cory Zanker)

We can also liquefy many gases by compressing them, if the temperature is not too high. The increased pressure brings the molecules of a gas closer together, such that the attractions between the molecules become strong relative to their KE. Consequently, they form liquids. Butane, C_4H_{10} , is the fuel used in disposable lighters and is a gas at standard temperature and pressure. Inside the lighter's fuel compartment, the butane is compressed to a pressure that results in its condensation to the liquid state, as shown in [\[link\]](#).



Gaseous butane is compressed within the storage compartment of a disposable lighter, resulting in its condensation to the liquid state.
(credit: modification of work by "Sam-Cat"/Flickr)

Finally, if the temperature of a liquid becomes sufficiently low, or the pressure on the liquid becomes sufficiently high, the molecules of the liquid no longer have enough KE to overcome the IMF between them, and a solid forms. A more thorough discussion of these and other changes of state, or phase transitions, is provided in a later module of this chapter.

Note:

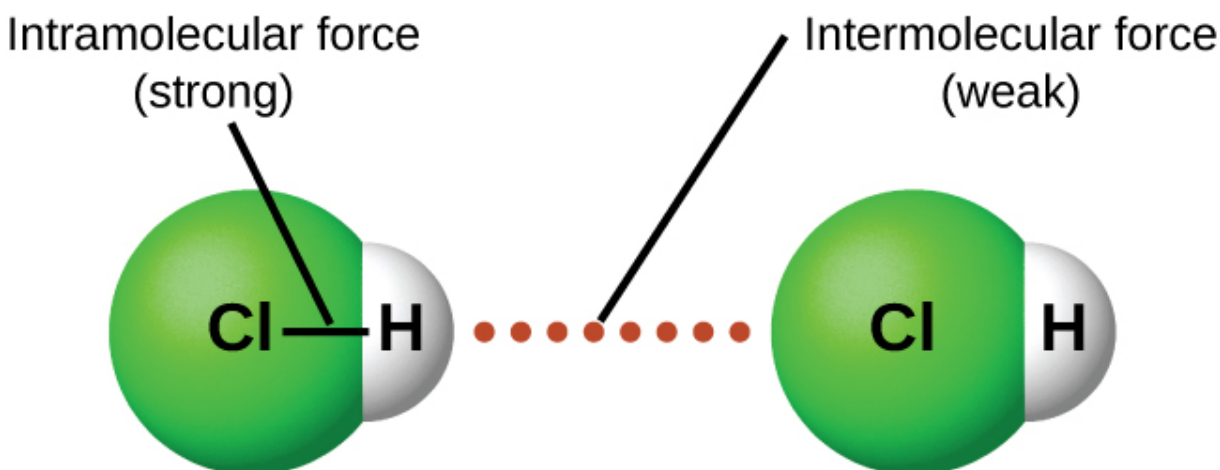


Access this [interactive simulation](#) on states of matter, phase transitions, and intermolecular forces. This simulation is useful for visualizing concepts introduced throughout this chapter.

Forces between Molecules

Under appropriate conditions, the attractions between all gas molecules will cause them to form liquids or solids. This is due to intermolecular forces, not *intramolecular* forces. *Intramolecular* forces are those *within* the molecule that keep the molecule together, for example, the bonds between the atoms. *Intermolecular* forces are the attractions *between* molecules, which determine many of the physical properties of a substance. [\[link\]](#) illustrates these different molecular forces. The strengths of these attractive forces vary widely, though usually the IMFs between small molecules are weak compared to the intramolecular forces that bond atoms together within a molecule. For example, to overcome the IMFs in one mole of

liquid HCl and convert it into gaseous HCl requires only about 17 kilojoules. However, to break the covalent bonds between the hydrogen and chlorine atoms in one mole of HCl requires about 25 times more energy—430 kilojoules.



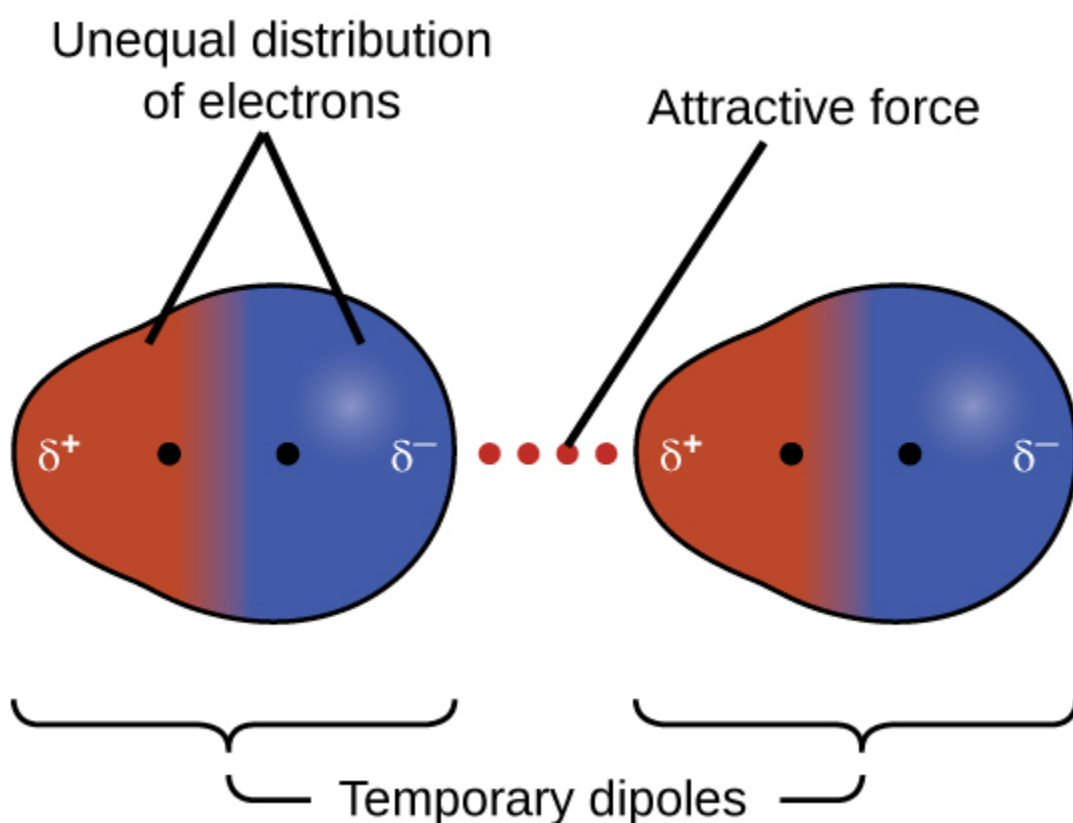
Intramolecular forces keep a molecule intact. Intermolecular forces hold multiple molecules together and determine many of a substance's properties.

All of the attractive forces between neutral atoms and molecules are known as **van der Waals forces**, although they are usually referred to more informally as intermolecular attraction. We will consider the various types of IMFs in the next three sections of this module.

Dispersion Forces

One of the three van der Waals forces is present in all condensed phases, regardless of the nature of the atoms or molecules composing the substance. This attractive force is called the London dispersion force in honor of German-born American physicist Fritz London who, in 1928, first explained it. This force is often referred to as simply the **dispersion force**. Because the electrons of an atom or molecule are in constant motion (or,

alternatively, the electron's location is subject to quantum-mechanical variability), at any moment in time, an atom or molecule can develop a temporary, **instantaneous dipole** if its electrons are distributed asymmetrically. The presence of this dipole can, in turn, distort the electrons of a neighboring atom or molecule, producing an **induced dipole**. These two rapidly fluctuating, temporary dipoles thus result in a relatively weak electrostatic attraction between the species—a so-called dispersion force like that illustrated in [\[link\]](#).



Dispersion forces result from the formation of temporary dipoles, as illustrated here for two nonpolar diatomic molecules.

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak,

however, and become significant only when the molecules are very close. Larger and heavier atoms and molecules exhibit stronger dispersion forces than do smaller and lighter atoms and molecules. F_2 and Cl_2 are gases at room temperature (reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in [\[link\]](#).

Melting and Boiling Points of the Halogens				
Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average,

farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as **polarizability**. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

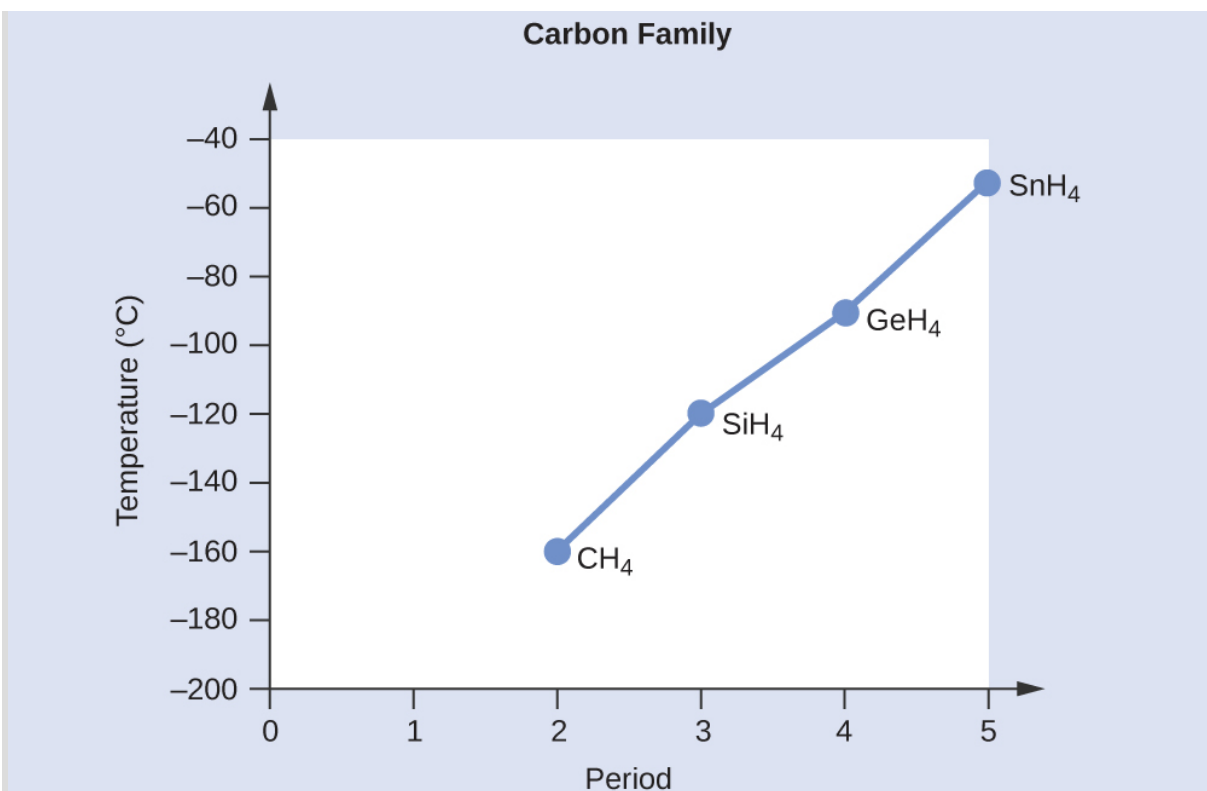
Example:**London Forces and Their Effects**

Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH_4 , SiH_4 , GeH_4 , and SnH_4 . Explain your reasoning.

Solution

Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of CH_4 , SiH_4 , GeH_4 , and SnH_4 are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH_4 is expected to have the lowest boiling point and SnH_4 the highest boiling point. The ordering from lowest to highest boiling point is expected to be $\text{CH}_4 < \text{SiH}_4 < \text{GeH}_4 < \text{SnH}_4$.

A graph of the actual boiling points of these compounds versus the period of the group 14 element shows this prediction to be correct:



Check Your Learning

Order the following hydrocarbons from lowest to highest boiling point: C₂H₆, C₃H₈, and C₄H₁₀.

Note:

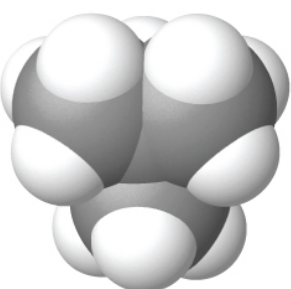
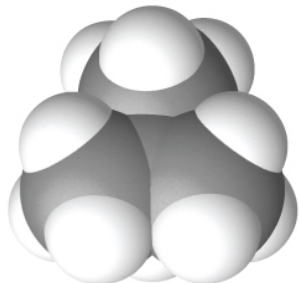
Answer:

C₂H₆ < C₃H₈ < C₄H₁₀. All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore C₂H₆ < C₃H₈ < C₄H₁₀.

The shapes of molecules also affect the magnitudes of the dispersion forces between them. For example, boiling points for the isomers *n*-pentane,

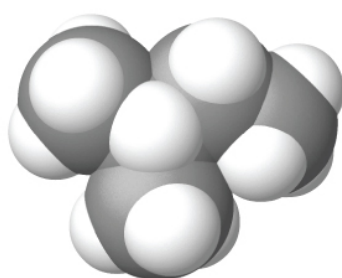
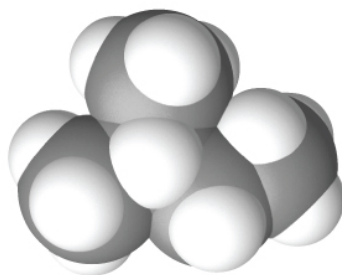
isopentane, and neopentane (shown in [\[link\]](#)) are 36 °C, 27 °C, and 9.5 °C, respectively. Even though these compounds are composed of molecules with the same chemical formula, C_5H_{12} , the difference in boiling points suggests that dispersion forces in the liquid phase are different, being greatest for *n*-pentane and least for neopentane. The elongated shape of *n*-pentane provides a greater surface area available for contact between molecules, resulting in correspondingly stronger dispersion forces. The more compact shape of isopentane offers a smaller surface area available for intermolecular contact and, therefore, weaker dispersion forces. Neopentane molecules are the most compact of the three, offering the least available surface area for intermolecular contact and, hence, the weakest dispersion forces. This behavior is analogous to the connections that may be formed between strips of VELCRO brand fasteners: the greater the area of the strip's contact, the stronger the connection.

Small contact area,
weakest attraction



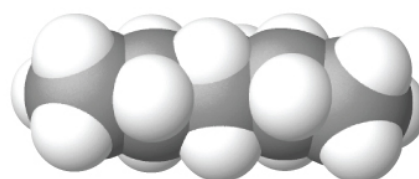
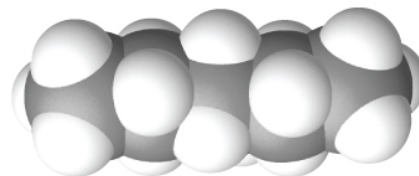
neopentane
boiling point: 9.5 °C

Less surface area,
less attraction



isopentane
boiling point: 27 °C

Large contact area,
strong attraction



n-pentane
boiling point: 36 °C

The strength of the dispersion forces increases with the contact area

between molecules, as demonstrated by the boiling points of these pentane isomers.

Note:

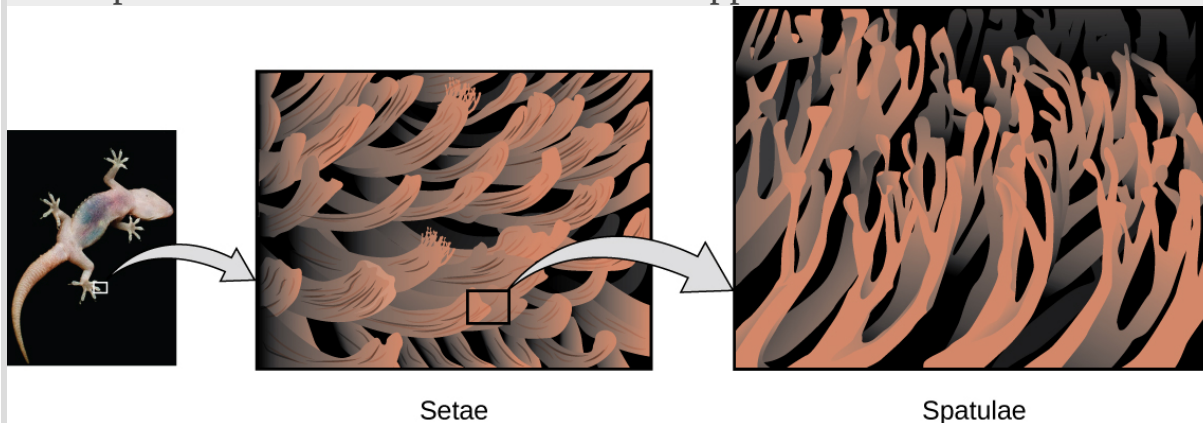
Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos' feet to behave this way.

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in [\[link\]](#), with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from “sticky” to “non-sticky.” Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally nonsticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily

move across it. Further investigations may eventually lead to the development of better adhesives and other applications.



Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off." (credit photo: modification of work by "JC*+A!"/Flickr)

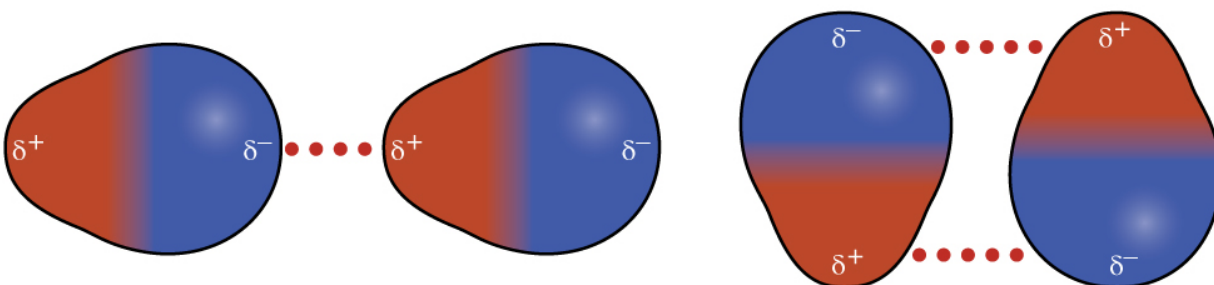
Note:



Watch this [video](#) to learn more about Kellar Autumn's research that determined that van der Waals forces are responsible for a gecko's ability to cling and climb.

Dipole-Dipole Attractions

Recall from the chapter on chemical bonding and molecular geometry that *polar* molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule—a separation of charge called a *dipole*. Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom bears the partial negative charge, whereas the less electronegative H atom bears the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attractive force is called a **dipole-dipole attraction**—the electrostatic force between the partially positive end of one polar molecule and the partially negative end of another, as illustrated in [\[link\]](#).



This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

The effect of a dipole-dipole attraction is apparent when we compare the properties of HCl molecules to nonpolar F_2 molecules. Both HCl and F_2 consist of the same number of atoms and have approximately the same molecular mass. At a temperature of 150 K, molecules of both substances would have the same average KE. However, the dipole-dipole attractions between HCl molecules are sufficient to cause them to “stick together” to form a liquid, whereas the relatively weaker dispersion forces between nonpolar F_2 molecules are not, and so this substance is gaseous at this

temperature. The higher normal boiling point of HCl (188 K) compared to F_2 (85 K) is a reflection of the greater strength of dipole-dipole attractions between HCl molecules, compared to the attractions between nonpolar F_2 molecules. We will often use values such as boiling or freezing points, or enthalpies of vaporization or fusion, as indicators of the relative strengths of IMFs of attraction present within different substances.

Example:**Dipole-Dipole Forces and Their Effects**

Predict which will have the higher boiling point: N_2 or CO. Explain your reasoning.

Solution

CO and N_2 are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because N_2 is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have the higher boiling point.

Check Your Learning

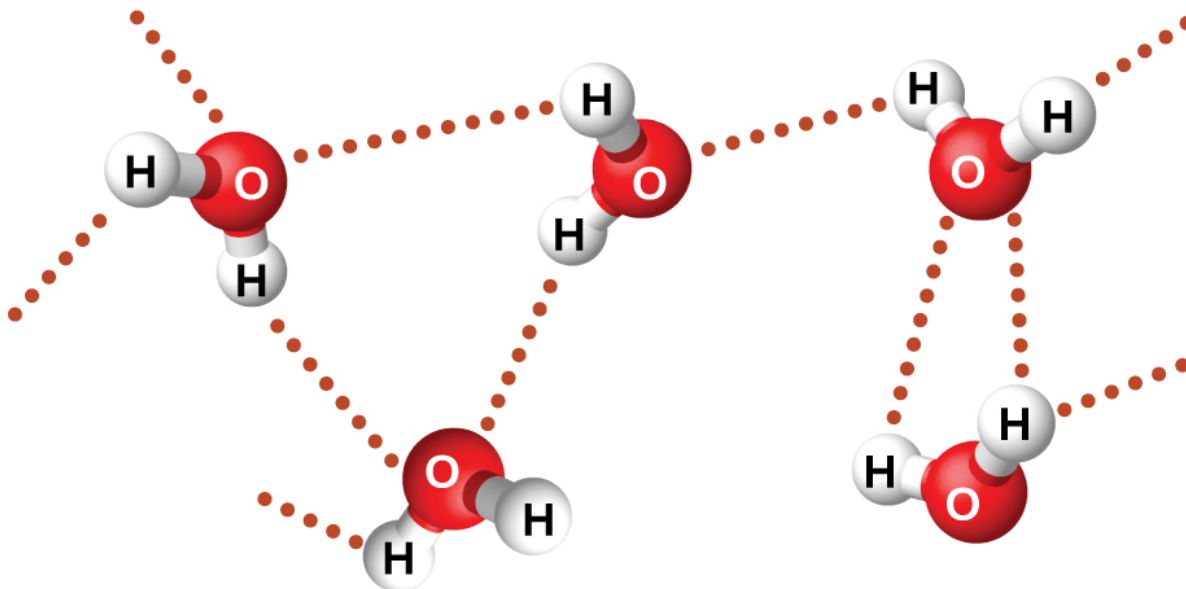
Predict which will have the higher boiling point: ICl or Br_2 . Explain your reasoning.

Note:**Answer:**

ICl. ICl and Br_2 have similar masses (~160 amu) and therefore experience similar London dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; Br_2 is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICl will have the higher boiling point.

Hydrogen Bonding

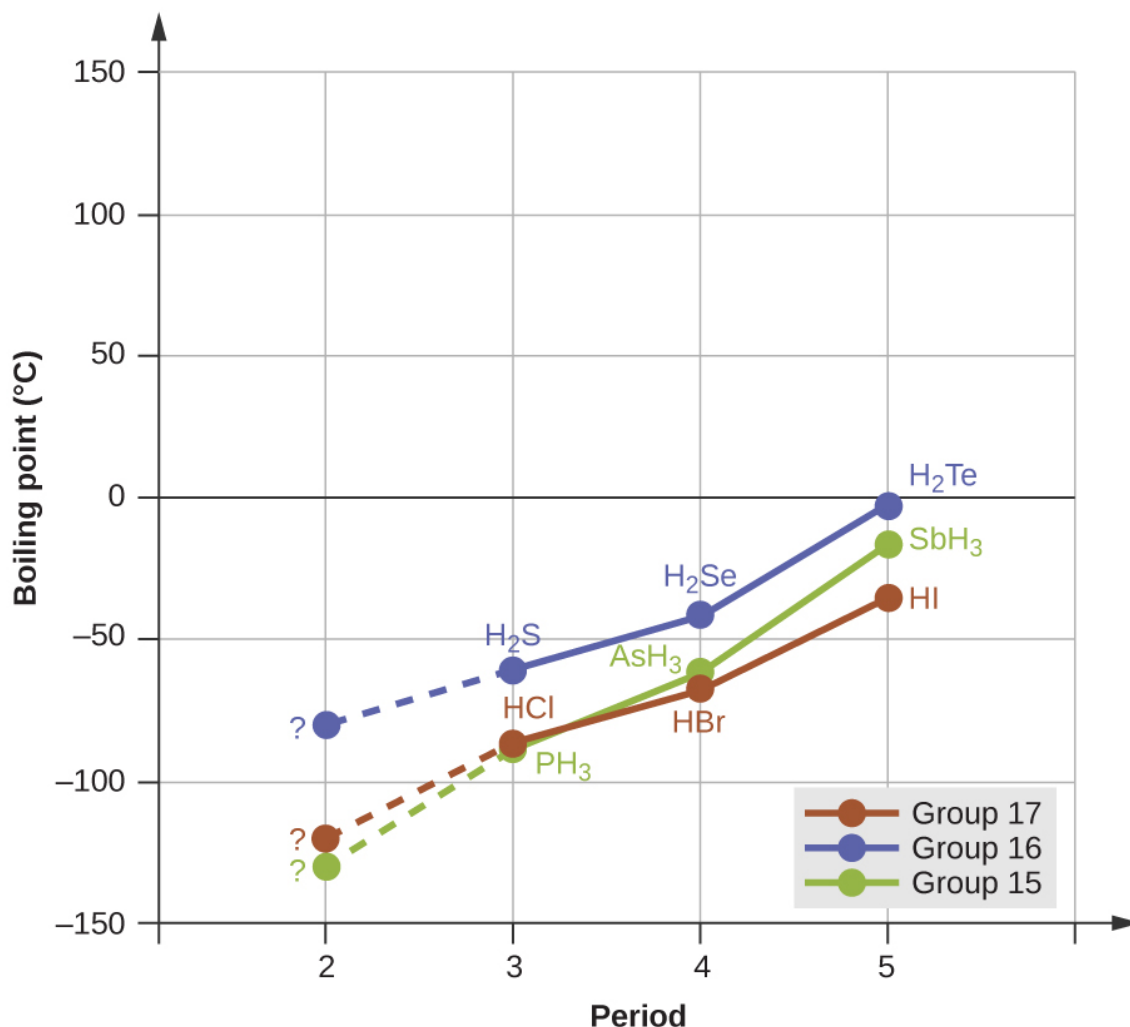
Nitrosyl fluoride (ONF, molecular mass 49 amu) is a gas at room temperature. Water (H₂O, molecular mass 18 amu) is a liquid, even though it has a lower molecular mass. We clearly cannot attribute this difference between the two compounds to dispersion forces. Both molecules have about the same shape and ONF is the heavier and larger molecule. It is, therefore, expected to experience more significant dispersion forces. Additionally, we cannot attribute this difference in boiling points to differences in the dipole moments of the molecules. Both molecules are polar and exhibit comparable dipole moments. The large difference between the boiling points is due to a particularly strong dipole-dipole attraction that may occur when a molecule contains a hydrogen atom bonded to a fluorine, oxygen, or nitrogen atom (the three most electronegative elements). The very large difference in electronegativity between the H atom (2.1) and the atom to which it is bonded (4.0 for an F atom, 3.5 for an O atom, or 3.0 for a N atom), combined with the very small size of a H atom and the relatively small sizes of F, O, or N atoms, leads to *highly concentrated partial charges* with these atoms. Molecules with F-H, O-H, or N-H moieties are very strongly attracted to similar moieties in nearby molecules, a particularly strong type of dipole-dipole attraction called **hydrogen bonding**. Examples of hydrogen bonds include HF \cdots HF, H₂O \cdots HOH, and H₃N \cdots HNH₂, in which the hydrogen bonds are denoted by dots. [\[link\]](#) illustrates hydrogen bonding between water molecules.



Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

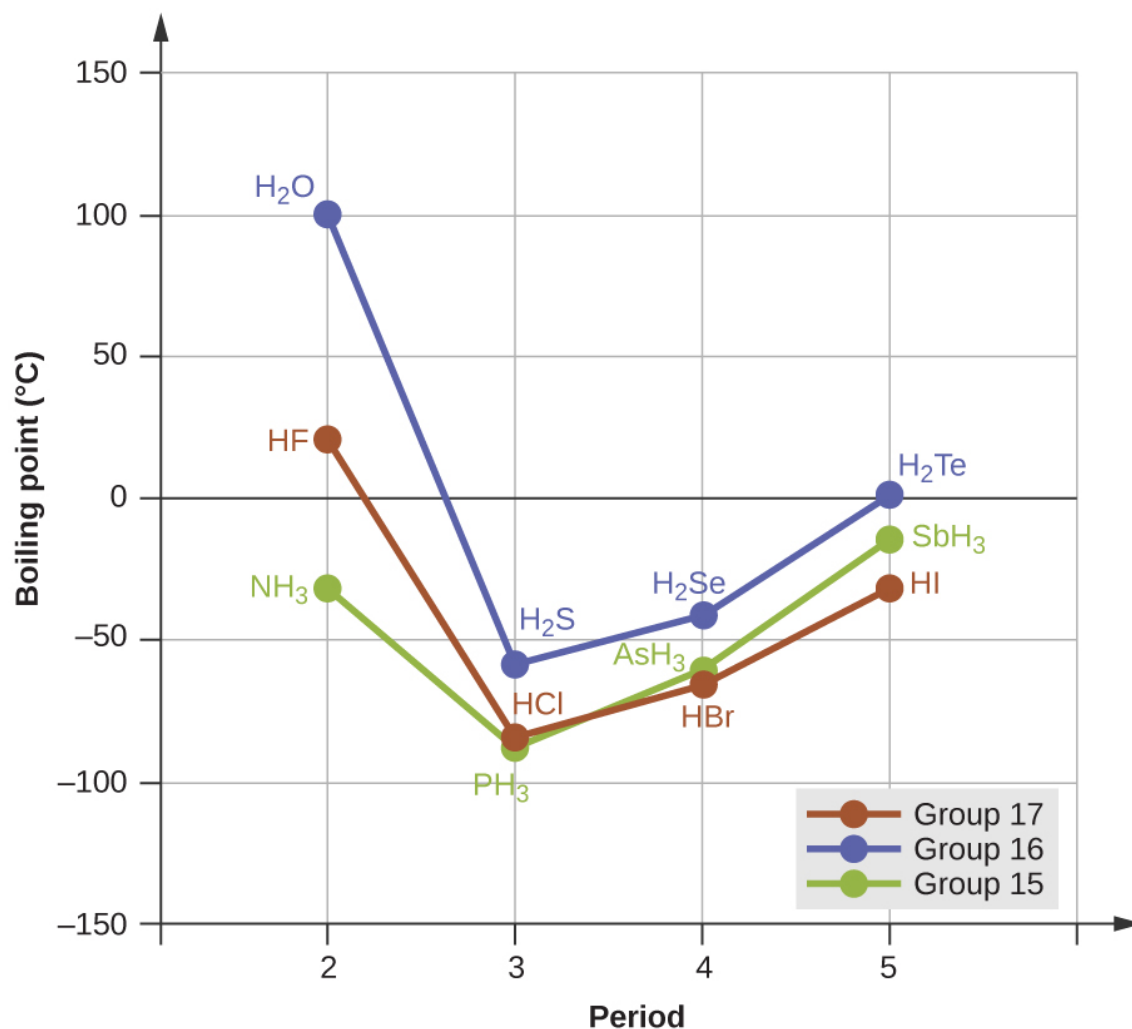
Despite use of the word “bond,” keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, only about 5 to 10% as strong, but are generally much stronger than other dipole-dipole attractions and dispersion forces.

Hydrogen bonds have a pronounced effect on the properties of condensed phases (liquids and solids). For example, consider the trends in boiling points for the binary hydrides of group 15 (NH_3 , PH_3 , AsH_3 , and SbH_3), group 16 hydrides (H_2O , H_2S , H_2Se , and H_2Te), and group 17 hydrides (HF , HCl , HBr , and HI). The boiling points of the heaviest three hydrides for each group are plotted in [\[link\]](#). As we progress down any of these groups, the polarities of the molecules decrease slightly, whereas the sizes of the molecules increase substantially. The effect of increasingly stronger dispersion forces dominates that of increasingly weaker dipole-dipole attractions, and the boiling points are observed to increase steadily.



For the group 15, 16, and 17 hydrides, the boiling points for each class of compounds increase with increasing molecular mass for elements in periods 3, 4, and 5.

If we use this trend to predict the boiling points for the lightest hydride for each group, we would expect NH_3 to boil at about -120°C , H_2O to boil at about -80°C , and HF to boil at about -110°C . However, when we measure the boiling points for these compounds, we find that they are dramatically higher than the trends would predict, as shown in [\[link\]](#). The stark contrast between our naïve predictions and reality provides compelling evidence for the strength of hydrogen bonding.



In comparison to periods 3–5, the binary hydrides of period 2 elements in groups 17, 16 and 15 (F, O and N, respectively) exhibit anomalously high boiling points due to hydrogen bonding.

Example:

Effect of Hydrogen Bonding on Boiling Points

Consider the compounds dimethylether (CH_3OCH_3), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), and propane ($\text{CH}_3\text{CH}_2\text{CH}_3$). Their boiling points, not

necessarily in order, are $-42.1\text{ }^{\circ}\text{C}$, $-24.8\text{ }^{\circ}\text{C}$, and $78.4\text{ }^{\circ}\text{C}$. Match each compound with its boiling point. Explain your reasoning.

Solution

The VSEPR-predicted shapes of CH_3OCH_3 , $\text{CH}_3\text{CH}_2\text{OH}$, and $\text{CH}_3\text{CH}_2\text{CH}_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $\text{CH}_3\text{CH}_2\text{CH}_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, $\text{CH}_3\text{CH}_2\text{OH}$ has an $-\text{OH}$ group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $\text{CH}_3\text{CH}_2\text{CH}_3 < \text{CH}_3\text{OCH}_3 < \text{CH}_3\text{CH}_2\text{OH}$. The boiling point of propane is $-42.1\text{ }^{\circ}\text{C}$, the boiling point of dimethylether is $-24.8\text{ }^{\circ}\text{C}$, and the boiling point of ethanol is $78.5\text{ }^{\circ}\text{C}$.

Check Your Learning

Ethane (CH_3CH_3) has a melting point of $-183\text{ }^{\circ}\text{C}$ and a boiling point of $-89\text{ }^{\circ}\text{C}$. Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Note:

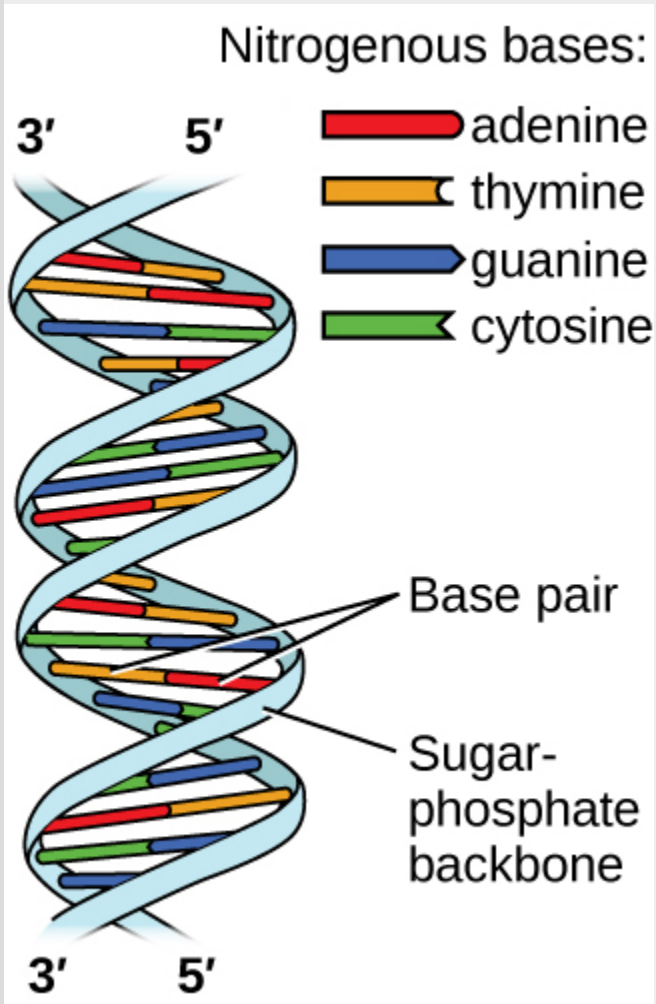
Answer:

The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an $-\text{NH}$ group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of $-93\text{ }^{\circ}\text{C}$ and a boiling point of $-6\text{ }^{\circ}\text{C}$.

Note:

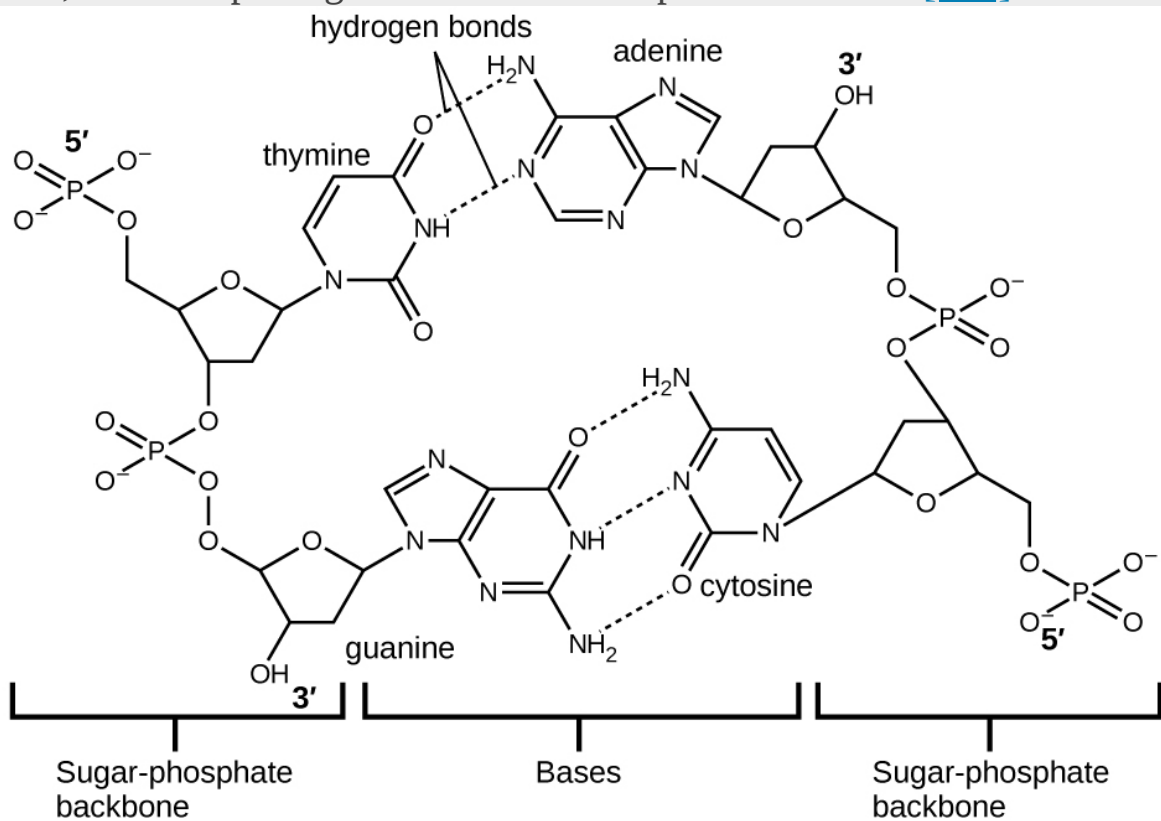
Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in [\[link\]](#).



Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure [\[link\]](#).



The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called “complementary base pairs.”

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily “unzip” down the middle since hydrogen bonds are

relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

Key Concepts and Summary

The physical properties of condensed matter (liquids and solids) can be explained in terms of the kinetic molecular theory. In a liquid, intermolecular attractive forces hold the molecules in contact, although they still have sufficient KE to move past each other.

Intermolecular attractive forces, collectively referred to as van der Waals forces, are responsible for the behavior of liquids and solids and are electrostatic in nature. Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one dipolar molecule for the partial positive end of another. The temporary dipole that results from the motion of the electrons in an atom can induce a dipole in an adjacent atom and give rise to the London dispersion force. London forces increase with increasing molecular size. Hydrogen bonds are a special type of dipole-dipole attraction that results when hydrogen is bonded to one of the three most electronegative elements: F, O, or N.

Chemistry End of Chapter Exercises

Exercise:

Problem:

In terms of their bulk properties, how do liquids and solids differ?
How are they similar?

Solution:

Liquids and solids are similar in that they are matter composed of atoms, ions, or molecules. They are incompressible and have similar

densities that are both much larger than those of gases. They are different in that liquids have no fixed shape, and solids are rigid.

Exercise:

Problem:

In terms of the kinetic molecular theory, in what ways are liquids similar to solids? In what ways are liquids different from solids?

Exercise:

Problem:

In terms of the kinetic molecular theory, in what ways are liquids similar to gases? In what ways are liquids different from gases?

Solution:

They are similar in that the atoms or molecules are free to move from one position to another. They differ in that the particles of a liquid are confined to the shape of the vessel in which they are placed. In contrast, a gas will expand without limit to fill the space into which it is placed.

Exercise:

Problem:

Explain why liquids assume the shape of any container into which they are poured, whereas solids are rigid and retain their shape.

Exercise:

Problem:

What is the evidence that all neutral atoms and molecules exert attractive forces on each other?

Solution:

All atoms and molecules will condense into a liquid or solid in which the attractive forces exceed the kinetic energy of the molecules, at sufficiently low temperature.

Exercise:

Problem:

Open the [PhET States of Matter Simulation](#) to answer the following questions:

(a) Select the Solid, Liquid, Gas tab. Explore by selecting different substances, heating and cooling the systems, and changing the state. What similarities do you notice between the four substances for each phase (solid, liquid, gas)? What differences do you notice?

(b) For each substance, select each of the states and record the given temperatures. How do the given temperatures for each state correlate with the strengths of their intermolecular attractions? Explain.

(c) Select the Interaction Potential tab, and use the default neon atoms. Move the Ne atom on the right and observe how the potential energy changes. Select the Total Force button, and move the Ne atom as before. When is the total force on each atom attractive and large enough to matter? Then select the Component Forces button, and move the Ne atom. When do the attractive (van der Waals) and repulsive (electron overlap) forces balance? How does this relate to the potential energy versus the distance between atoms graph? Explain.

Exercise:

Problem: Define the following and give an example of each:

(a) dispersion force

(b) dipole-dipole attraction

(c) hydrogen bond

Solution:

(a) Dispersion forces occur as an atom develops a temporary dipole moment when its electrons are distributed asymmetrically about the nucleus. This structure is more prevalent in large atoms such as argon or radon. A second atom can then be distorted by the appearance of the dipole in the first atom. The electrons of the second atom are attracted toward the positive end of the first atom, which sets up a dipole in the second atom. The net result is rapidly fluctuating, temporary dipoles that attract one another (example: Ar). (b) A dipole-dipole attraction is a force that results from an electrostatic attraction of the positive end of one polar molecule for the negative end of another polar molecule (example: ICl molecules attract one another by dipole-dipole interaction). (c) Hydrogen bonds form whenever a hydrogen atom is bonded to one of the more electronegative atoms, such as a fluorine, oxygen, or nitrogen atom. The electrostatic attraction between the partially positive hydrogen atom in one molecule and the partially negative atom in another molecule gives rise to a strong dipole-dipole interaction called a hydrogen bond (example: $\text{HF} \cdots \text{HF}$).

Exercise:**Problem:**

The types of intermolecular forces in a substance are identical whether it is a solid, a liquid, or a gas. Why then does a substance change phase from a gas to a liquid or to a solid?

Exercise:**Problem:**

Why do the boiling points of the noble gases increase in the order $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$?

Solution:

The London forces typically increase as the number of electrons increase.

Exercise:**Problem:**

Neon and HF have approximately the same molecular masses.

- (a) Explain why the boiling points of Neon and HF differ.
- (b) Compare the change in the boiling points of Ne, Ar, Kr, and Xe with the change of the boiling points of HF, HCl, HBr, and HI, and explain the difference between the changes with increasing atomic or molecular mass.

Exercise:**Problem:**

Arrange each of the following sets of compounds in order of increasing boiling point temperature:

- (a) HCl, H₂O, SiH₄
- (b) F₂, Cl₂, Br₂
- (c) CH₄, C₂H₆, C₃H₈
- (d) O₂, NO, N₂

Solution:

(a) SiH₄ < HCl < H₂O; (b) F₂ < Cl₂ < Br₂; (c) CH₄ < C₂H₆ < C₃H₈; (d) N₂ < O₂ < NO

Exercise:**Problem:**

The molecular mass of butanol, C₄H₉OH, is 74.14; that of ethylene glycol, CH₂(OH)CH₂OH, is 62.08, yet their boiling points are 117.2 °C and 174 °C, respectively. Explain the reason for the difference.

Exercise:

Problem:

On the basis of intermolecular attractions, explain the differences in the boiling points of *n*-butane ($-1\text{ }^{\circ}\text{C}$) and chloroethane ($12\text{ }^{\circ}\text{C}$), which have similar molar masses.

Solution:

Only rather small dipole-dipole interactions from C-H bonds are available to hold *n*-butane in the liquid state. Chloroethane, however, has rather large dipole interactions because of the Cl-C bond; the interaction is therefore stronger, leading to a higher boiling point.

Exercise:**Problem:**

On the basis of dipole moments and/or hydrogen bonding, explain in a qualitative way the differences in the boiling points of acetone ($56.2\text{ }^{\circ}\text{C}$) and 1-propanol ($97.4\text{ }^{\circ}\text{C}$), which have similar molar masses.

Exercise:**Problem:**

The melting point of $\text{H}_2\text{O}(\text{s})$ is $0\text{ }^{\circ}\text{C}$. Would you expect the melting point of $\text{H}_2\text{S}(\text{s})$ to be $-85\text{ }^{\circ}\text{C}$, $0\text{ }^{\circ}\text{C}$, or $185\text{ }^{\circ}\text{C}$? Explain your answer.

Solution:

$-85\text{ }^{\circ}\text{C}$. Water has stronger hydrogen bonds so it melts at a higher temperature.

Exercise:**Problem:**

Silane (SiH_4), phosphine (PH_3), and hydrogen sulfide (H_2S) melt at $-185\text{ }^{\circ}\text{C}$, $-133\text{ }^{\circ}\text{C}$, and $-85\text{ }^{\circ}\text{C}$, respectively. What does this suggest about the polar character and intermolecular attractions of the three compounds?

Exercise:**Problem:**

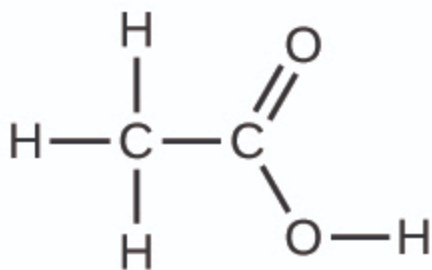
Explain why a hydrogen bond between two water molecules is weaker than a hydrogen bond between two hydrogen fluoride molecules.

Solution:

The hydrogen bond between two hydrogen fluoride molecules is stronger than that between two water molecules because the electronegativity of F is greater than that of O. Consequently, the partial negative charge on F is greater than that on O. The hydrogen bond between the partially positive H and the larger partially negative F will be stronger than that formed between H and O.

Exercise:**Problem:**

Under certain conditions, molecules of acetic acid, CH_3COOH , form “dimers,” pairs of acetic acid molecules held together by strong intermolecular attractions:

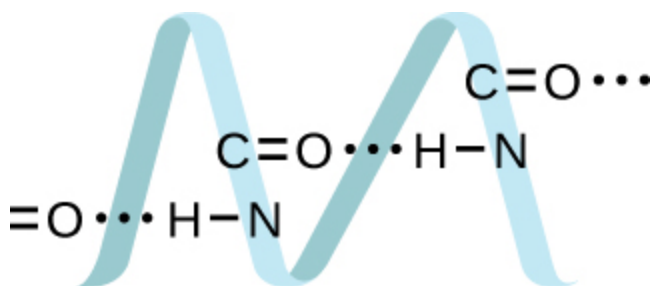


Draw a dimer of acetic acid, showing how two CH_3COOH molecules are held together, and stating the type of IMF that is responsible.

Exercise:

Problem:

Proteins are chains of amino acids that can form in a variety of arrangements, one of which is a helix. What kind of IMF is responsible for holding the protein strand in this shape? On the protein image, show the locations of the IMFs that hold the protein together:

**Solution:**

H-bonding is the principle IMF holding the protein strands together. The H-bonding is between the $\text{N}-\text{H}$ and $\text{C}=\text{O}$.

Exercise:**Problem:**

The density of liquid NH_3 is 0.64 g/mL; the density of gaseous NH_3 at STP is 0.0007 g/mL. Explain the difference between the densities of these two phases.

Exercise:**Problem:**

Identify the intermolecular forces present in the following solids:

- (a) $\text{CH}_3\text{CH}_2\text{OH}$
- (b) $\text{CH}_3\text{CH}_2\text{CH}_3$
- (c) $\text{CH}_3\text{CH}_2\text{Cl}$

Solution:

- (a) hydrogen bonding, dipole-dipole attraction, and dispersion forces;
- (b) dispersion forces; (c) dipole-dipole attraction and dispersion forces

Glossary

dipole-dipole attraction

intermolecular attraction between two permanent dipoles

dispersion force

(also, London dispersion force) attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together

hydrogen bonding

occurs when exceptionally strong dipoles attract; bonding that exists when hydrogen is bonded to one of the three most electronegative elements: F, O, or N

induced dipole

temporary dipole formed when the electrons of an atom or molecule are distorted by the instantaneous dipole of a neighboring atom or molecule

instantaneous dipole

temporary dipole that occurs for a brief moment in time when the electrons of an atom or molecule are distributed asymmetrically

intermolecular force

noncovalent attractive force between atoms, molecules, and/or ions

polarizability

measure of the ability of a charge to distort a molecule's charge distribution (electron cloud)

van der Waals force

attractive or repulsive force between molecules, including dipole-dipole, dipole-induced dipole, and London dispersion forces; does not include forces due to covalent or ionic bonding, or the attraction between ions and molecules

Properties of Liquids

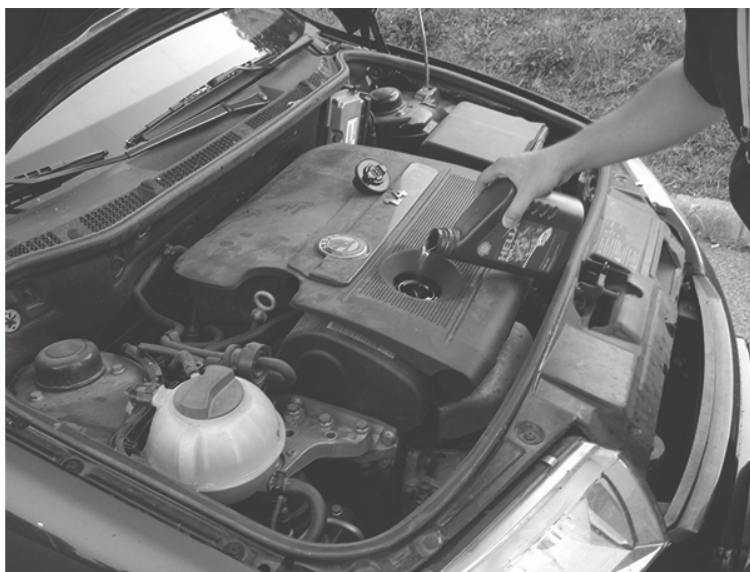
By the end of this section, you will be able to:

- Distinguish between adhesive and cohesive forces
- Define viscosity, surface tension, and capillary rise
- Describe the roles of intermolecular attractive forces in each of these properties/phenomena

When you pour a glass of water, or fill a car with gasoline, you observe that water and gasoline flow freely. But when you pour syrup on pancakes or add oil to a car engine, you note that syrup and motor oil do not flow as readily. The **viscosity** of a liquid is a measure of its resistance to flow. Water, gasoline, and other liquids that flow freely have a low viscosity. Honey, syrup, motor oil, and other liquids that do not flow freely, like those shown in [\[link\]](#), have higher viscosities. We can measure viscosity by measuring the rate at which a metal ball falls through a liquid (the ball falls more slowly through a more viscous liquid) or by measuring the rate at which a liquid flows through a narrow tube (more viscous liquids flow more slowly).



(a)



(b)

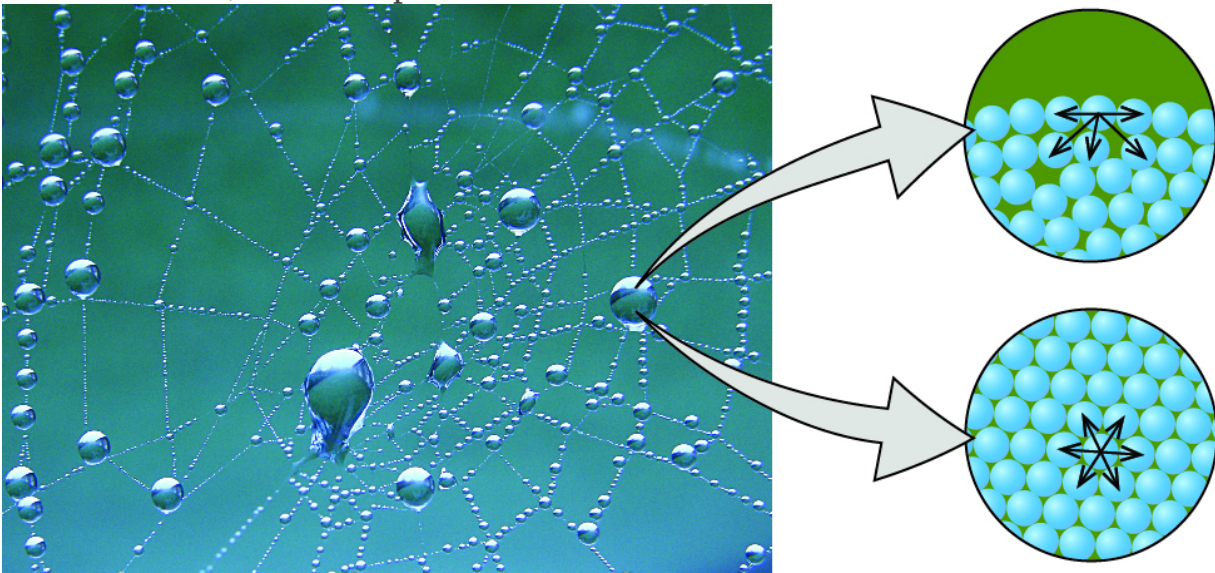
(a) Honey and (b) motor oil are examples of liquids with high viscosities; they flow slowly. (credit a: modification of work by Scott Bauer; credit b: modification of work by David Nagy)

The IMFs between the molecules of a liquid, the size and shape of the molecules, and the temperature determine how easily a liquid flows. As [\[link\]](#) shows, the more structurally complex are the molecules in a liquid and the stronger the IMFs between them, the more difficult it is for them to move past each other and the greater is the viscosity of the liquid. As the temperature increases, the molecules move more rapidly and their kinetic energies are better able to overcome the forces that hold them together; thus, the viscosity of the liquid decreases.

Viscosities of Common Substances at 25 °C		
Substance	Formula	Viscosity (mPa·s)
water	H ₂ O	0.890
mercury	Hg	1.526
ethanol	C ₂ H ₅ OH	1.074
octane	C ₈ H ₁₈	0.508
ethylene glycol	CH ₂ (OH)CH ₂ (OH)	16.1
honey	variable	~2,000–10,000
motor oil	variable	~50–500

The various IMFs between identical molecules of a substance are examples of **cohesive forces**. The molecules within a liquid are surrounded by other molecules and are attracted equally in all directions by the cohesive forces

within the liquid. However, the molecules on the surface of a liquid are attracted only by about one-half as many molecules. Because of the unbalanced molecular attractions on the surface molecules, liquids contract to form a shape that minimizes the number of molecules on the surface—that is, the shape with the minimum surface area. A small drop of liquid tends to assume a spherical shape, as shown in [\[link\]](#), because in a sphere, the ratio of surface area to volume is at a minimum. Larger drops are more greatly affected by gravity, air resistance, surface interactions, and so on, and as a result, are less spherical.

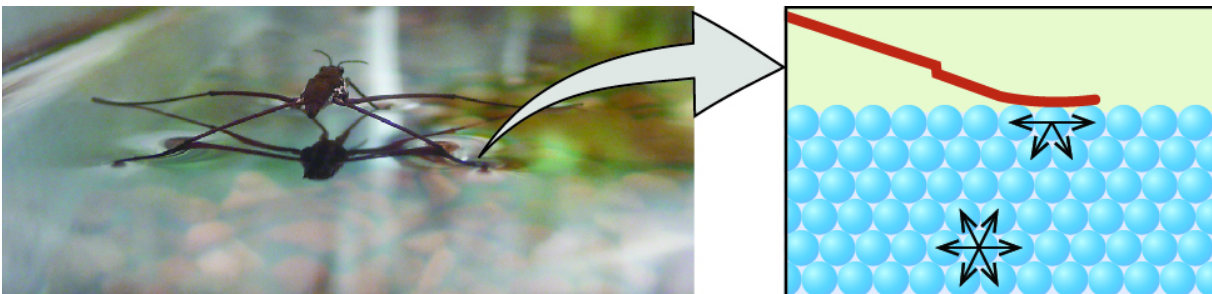


Attractive forces result in a spherical water drop that minimizes surface area; cohesive forces hold the sphere together; adhesive forces keep the drop attached to the web. (credit photo: modification of work by “OliBac”/Flickr)

Surface tension is defined as the energy required to increase the surface area of a liquid, or the force required to increase the length of a liquid surface by a given amount. This property results from the cohesive forces between molecules at the surface of a liquid, and it causes the surface of a liquid to behave like a stretched rubber membrane. Surface tensions of several liquids are presented in [\[link\]](#). Among common liquids, water exhibits a distinctly high surface tension due to strong hydrogen bonding between its molecules. As a result of this high surface tension, the surface

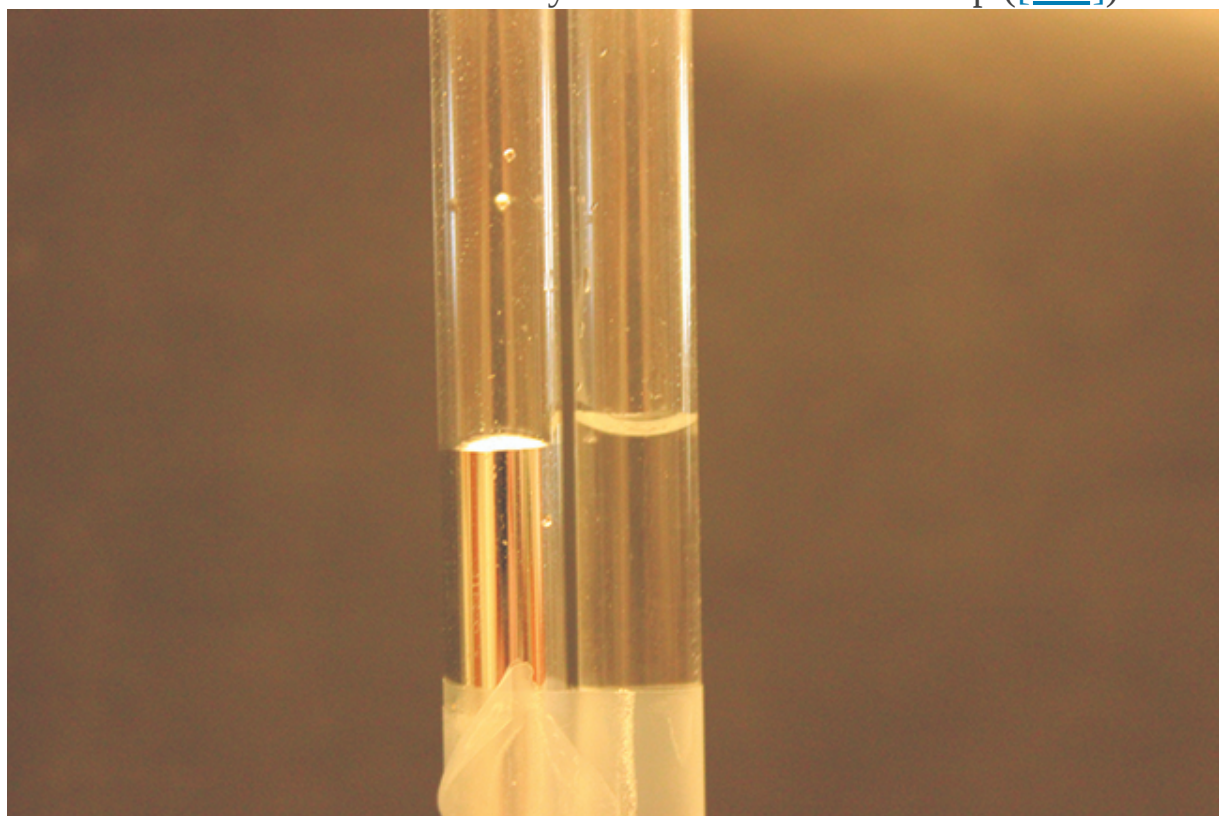
of water represents a relatively “tough skin” that can withstand considerable force without breaking. A steel needle carefully placed on water will float. Some insects, like the one shown in [\[link\]](#), even though they are denser than water, move on its surface because they are supported by the surface tension.

Surface Tensions of Common Substances at 25 °C		
Substance	Formula	Surface Tension (mN/m)
water	H ₂ O	71.99
mercury	Hg	458.48
ethanol	C ₂ H ₅ OH	21.97
octane	C ₈ H ₁₈	21.14
ethylene glycol	CH ₂ (OH)CH ₂ (OH)	47.99



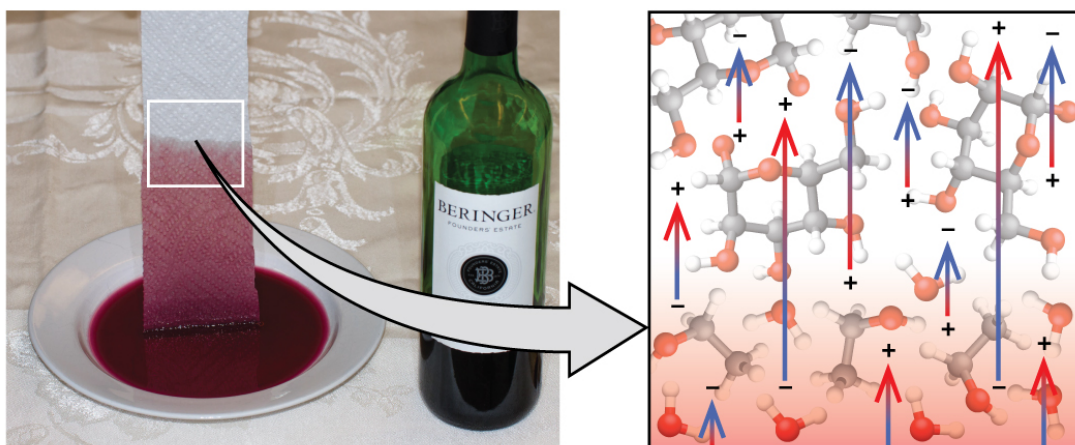
Surface tension (right) prevents this insect, a “water strider,” from sinking into the water.

The IMFs of attraction between two *different* molecules are called **adhesive forces**. Consider what happens when water comes into contact with some surface. If the adhesive forces between water molecules and the molecules of the surface are weak compared to the cohesive forces between the water molecules, the water does not “wet” the surface. For example, water does not wet waxed surfaces or many plastics such as polyethylene. Water forms drops on these surfaces because the cohesive forces within the drops are greater than the adhesive forces between the water and the plastic. Water spreads out on glass because the adhesive force between water and glass is greater than the cohesive forces within the water. When water is confined in a glass tube, its meniscus (surface) has a concave shape because the water wets the glass and creeps up the side of the tube. On the other hand, the cohesive forces between mercury atoms are much greater than the adhesive forces between mercury and glass. Mercury therefore does not wet glass, and it forms a convex meniscus when confined in a tube because the cohesive forces within the mercury tend to draw it into a drop ([\[link\]](#)).



Differences in the relative strengths of cohesive and adhesive forces result in different meniscus shapes for mercury (left) and water (right) in glass tubes. (credit: Mark Ott)

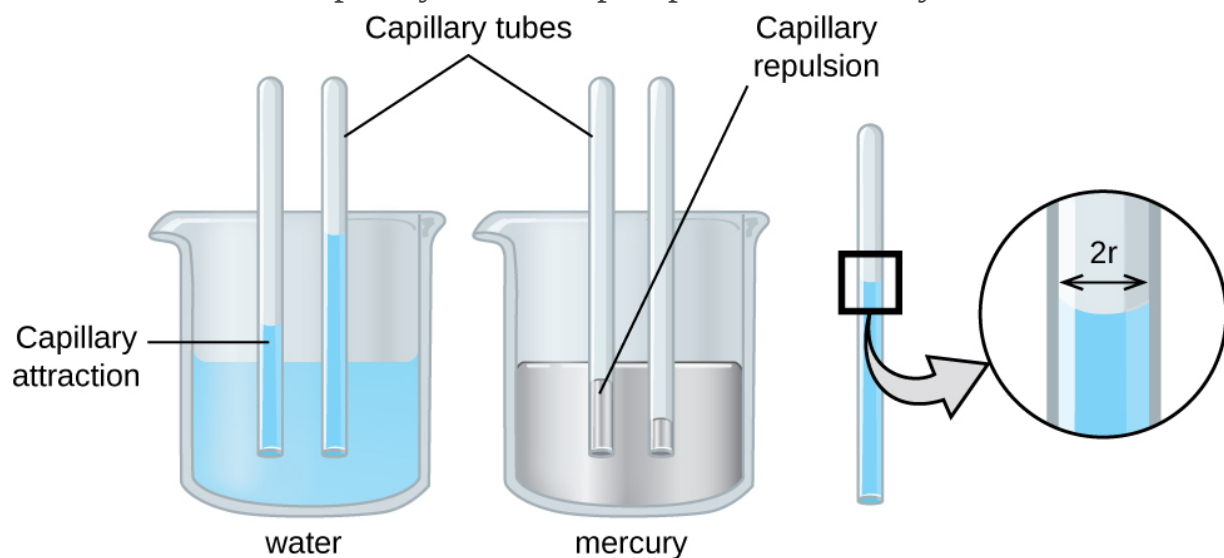
If you place one end of a paper towel in spilled wine, as shown in [\[link\]](#), the liquid wicks up the paper towel. A similar process occurs in a cloth towel when you use it to dry off after a shower. These are examples of **capillary action**—when a liquid flows within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules. The adhesive forces between the liquid and the porous material, combined with the cohesive forces within the liquid, may be strong enough to move the liquid upward against gravity.



Wine wicks up a paper towel (left) because of the strong attractions of water (and ethanol) molecules to the -OH groups on the towel's cellulose fibers and the strong attractions of water molecules to other water (and ethanol) molecules (right). (credit photo: modification of work by Mark Blaser)

Towels soak up liquids like water because the fibers of a towel are made of molecules that are attracted to water molecules. Most cloth towels are made of cotton, and paper towels are generally made from paper pulp. Both consist of long molecules of cellulose that contain many -OH groups. Water molecules are attracted to these -OH groups and form hydrogen bonds with them, which draws the H_2O molecules up the cellulose molecules. The water molecules are also attracted to each other, so large amounts of water are drawn up the cellulose fibers.

Capillary action can also occur when one end of a small diameter tube is immersed in a liquid, as illustrated in [\[link\]](#). If the liquid molecules are strongly attracted to the tube molecules, the liquid creeps up the inside of the tube until the weight of the liquid and the adhesive forces are in balance. The smaller the diameter of the tube is, the higher the liquid climbs. It is partly by capillary action occurring in plant cells called xylem that water and dissolved nutrients are brought from the soil up through the roots and into a plant. Capillary action is the basis for thin layer chromatography, a laboratory technique commonly used to separate small quantities of mixtures. You depend on a constant supply of tears to keep your eyes lubricated and on capillary action to pump tear fluid away.



Depending upon the relative strengths of adhesive and cohesive forces, a liquid may rise (such as water) or fall (such as mercury) in a glass capillary tube. The extent of the rise (or fall) is directly proportional to

the surface tension of the liquid and inversely proportional to the density of the liquid and the radius of the tube.

The height to which a liquid will rise in a capillary tube is determined by several factors as shown in the following equation:

Equation:

$$h = \frac{2T \cos \theta}{r\rho g}$$

In this equation, h is the height of the liquid inside the capillary tube relative to the surface of the liquid outside the tube, T is the surface tension of the liquid, θ is the contact angle between the liquid and the tube, r is the radius of the tube, ρ is the density of the liquid, and g is the acceleration due to gravity, 9.8 m/s^2 . When the tube is made of a material to which the liquid molecules are strongly attracted, they will spread out completely on the surface, which corresponds to a contact angle of 0° . This is the situation for water rising in a glass tube.

Example:

Capillary Rise

At 25°C , how high will water rise in a glass capillary tube with an inner diameter of 0.25 mm ?

For water, $T = 71.99 \text{ mN/m}$ and $\rho = 1.0 \text{ g/cm}^3$.

Solution

The liquid will rise to a height h given by: $h = \frac{2T \cos \theta}{r\rho g}$

The Newton is defined as a kg m/s^2 , and so the provided surface tension is equivalent to 0.07199 kg/s^2 . The provided density must be converted into units that will cancel appropriately: $\rho = 1000 \text{ kg/m}^3$. The diameter of the tube in meters is 0.00025 m , so the radius is 0.000125 m . For a glass tube immersed in water, the contact angle is $\theta = 0^\circ$, so $\cos \theta = 1$. Finally, acceleration due to gravity on the earth is $g = 9.8 \text{ m/s}^2$. Substituting these values into the equation, and cancelling units, we have:

Equation:

$$h = \frac{2 \left(0.07199 \text{ kg/s}^2 \right)}{(0.000125 \text{ m}) \left(1000 \text{ kg/m}^3 \right) \left(9.8 \text{ m/s}^2 \right)} = 0.12 \text{ m} = 12 \text{ cm}$$

Check Your Learning

Water rises in a glass capillary tube to a height of 8.4 cm. What is the diameter of the capillary tube?

Note:**Answer:**

diameter = 0.36 mm

Note:**Biomedical Applications of Capillary Action**

Many medical tests require drawing a small amount of blood, for example to determine the amount of glucose in someone with diabetes or the hematocrit level in an athlete. This procedure can be easily done because of capillary action, the ability of a liquid to flow up a small tube against gravity, as shown in [\[link\]](#). When your finger is pricked, a drop of blood forms and holds together due to surface tension—the unbalanced intermolecular attractions at the surface of the drop. Then, when the open end of a narrow-diameter glass tube touches the drop of blood, the adhesive forces between the molecules in the blood and those at the glass surface draw the blood up the tube. How far the blood goes up the tube depends on the diameter of the tube (and the type of fluid). A small tube has a relatively large surface area for a given volume of blood, which results in larger (relative) attractive forces, allowing the blood to be drawn farther up the tube. The liquid itself is held together by its own cohesive

forces. When the weight of the liquid in the tube generates a downward force equal to the upward force associated with capillary action, the liquid stops rising.



Blood is collected for medical analysis by capillary action, which draws blood into a small diameter glass tube. (credit: modification of work by Centers for Disease Control and Prevention)

Key Concepts and Summary

The intermolecular forces between molecules in the liquid state vary depending upon their chemical identities and result in corresponding variations in various physical properties. Cohesive forces between like molecules are responsible for a liquid's viscosity (resistance to flow) and surface tension (elasticity of a liquid surface). Adhesive forces between the molecules of a liquid and different molecules composing a surface in contact with the liquid are responsible for phenomena such as surface wetting and capillary rise.

Key Equations

- $h = \frac{2T \cos \theta}{r\rho g}$

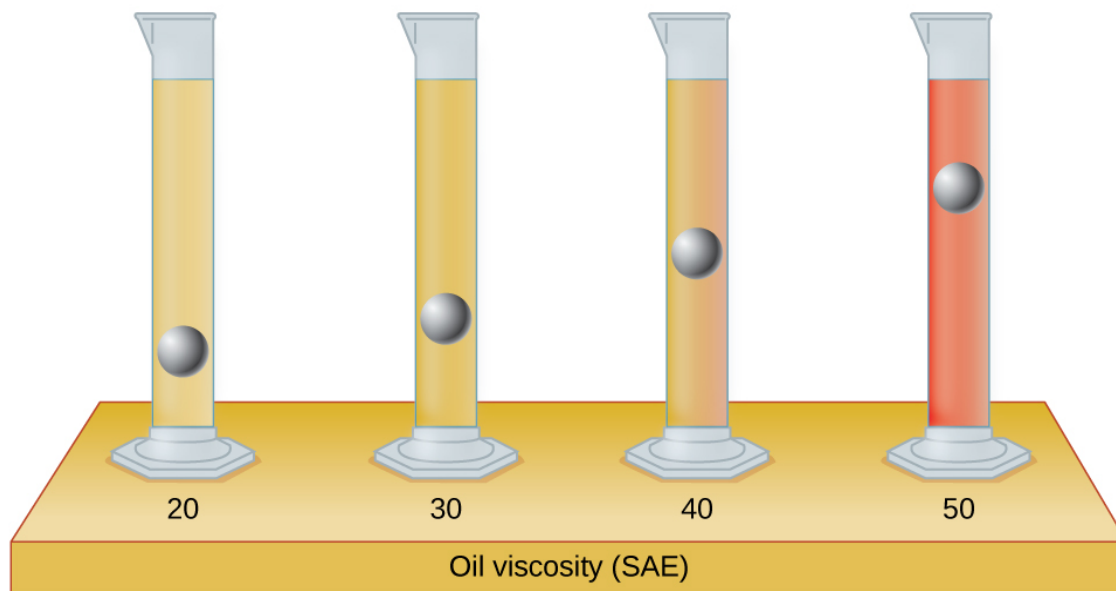
Chemistry End of Chapter Exercises

Exercise:

Problem:

The test tubes shown here contain equal amounts of the specified motor oils. Identical metal spheres were dropped at the same time into each of the tubes, and a brief moment later, the spheres had fallen to the heights indicated in the illustration.

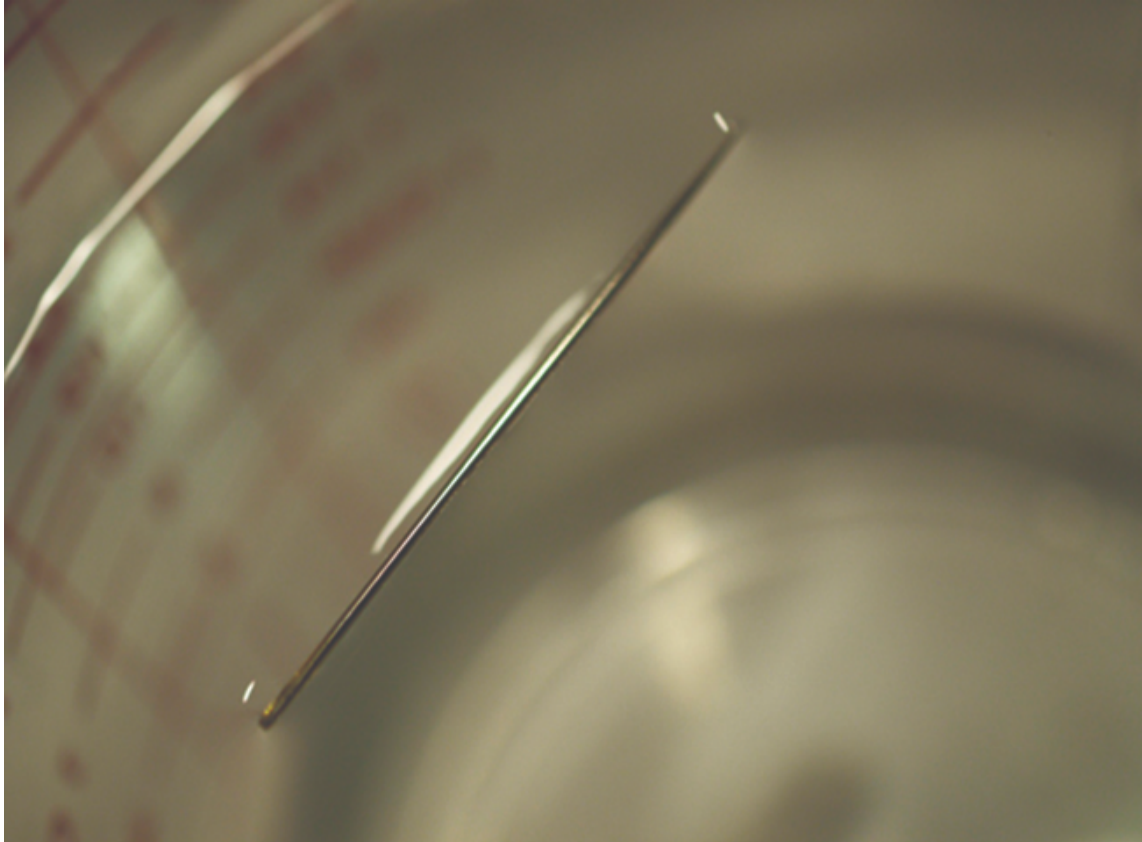
Rank the motor oils in order of increasing viscosity, and explain your reasoning:



Exercise:

Problem:

Although steel is denser than water, a steel needle or paper clip placed carefully lengthwise on the surface of still water can be made to float. Explain at a molecular level how this is possible:



(credit: Cory Zanker)

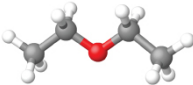
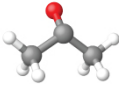
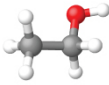
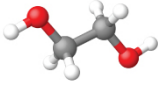
Solution:

The water molecules have strong intermolecular forces of hydrogen bonding. The water molecules are thus attracted strongly to one another and exhibit a relatively large surface tension, forming a type of “skin” at its surface. This skin can support a bug or paper clip if gently placed on the water.

Exercise:

Problem:

The surface tension and viscosity values for diethyl ether, acetone, ethanol, and ethylene glycol are shown here.

Compound	Molecule	Surface Tension (mN/m)	Viscosity (mPa s)
diethyl ether $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$		17	0.22
acetone CH_3COCH_3		23	0.31
ethanol $\text{C}_2\text{H}_5\text{OH}$		22	1.07
ethylene glycol $\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})$		48	16.1

(a) Explain their differences in viscosity in terms of the size and shape of their molecules and their IMFs.

(b) Explain their differences in surface tension in terms of the size and shape of their molecules and their IMFs:

Exercise:**Problem:**

You may have heard someone use the figure of speech “slower than molasses in winter” to describe a process that occurs slowly. Explain why this is an apt idiom, using concepts of molecular size and shape, molecular interactions, and the effect of changing temperature.

Solution:

Temperature has an effect on intermolecular forces: the higher the temperature, the greater the kinetic energies of the molecules and the greater the extent to which their intermolecular forces are overcome, and so the more fluid (less viscous) the liquid; the lower the

temperature, the lesser the intermolecular forces are overcome, and so the less viscous the liquid.

Exercise:

Problem:

It is often recommended that you let your car engine run idle to warm up before driving, especially on cold winter days. While the benefit of prolonged idling is dubious, it is certainly true that a warm engine is more fuel efficient than a cold one. Explain the reason for this.

Exercise:

Problem:

The surface tension and viscosity of water at several different temperatures are given in this table.

Water	Surface Tension (mN/m)	Viscosity (mPa s)
0 °C	75.6	1.79
20 °C	72.8	1.00
60 °C	66.2	0.47
100 °C	58.9	0.28

(a) As temperature increases, what happens to the surface tension of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.

(b) As temperature increases, what happens to the viscosity of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.

Solution:

(a) As the water reaches higher temperatures, the increased kinetic energies of its molecules are more effective in overcoming hydrogen bonding, and so its surface tension decreases. Surface tension and intermolecular forces are directly related. (b) The same trend in viscosity is seen as in surface tension, and for the same reason.

Exercise:

Problem:

At 25 °C, how high will water rise in a glass capillary tube with an inner diameter of 0.63 mm? Refer to [\[link\]](#) for the required information.

Exercise:

Problem:

Water rises in a glass capillary tube to a height of 17 cm. What is the diameter of the capillary tube?

Solution:

$$1.9 \times 10^{-4} \text{ m}$$

Glossary

adhesive force

force of attraction between molecules of different chemical identities

capillary action

flow of liquid within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid

molecules

cohesive force

force of attraction between identical molecules

surface tension

energy required to increase the area, or length, of a liquid surface by a given amount

viscosity

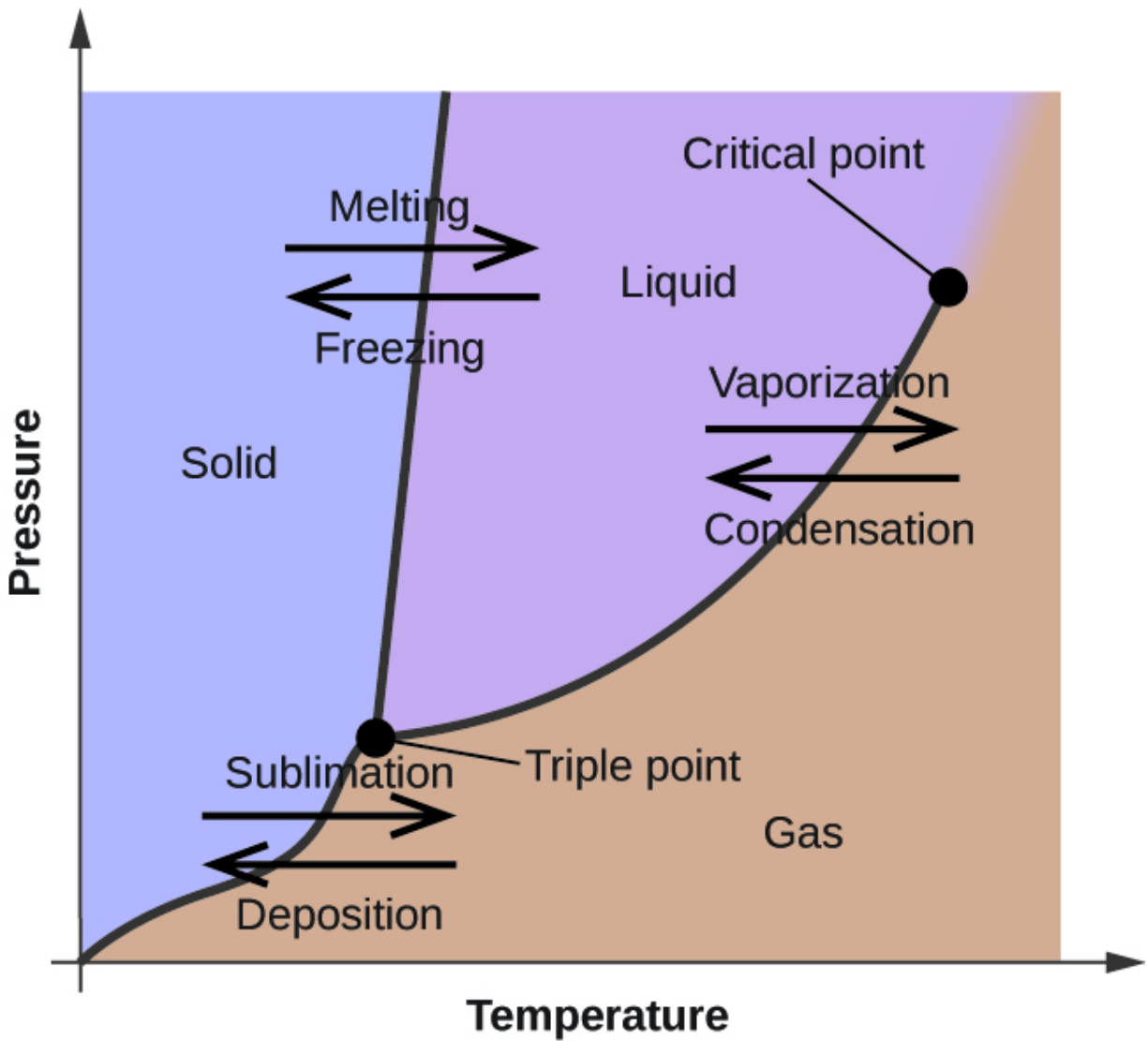
measure of a liquid's resistance to flow

Phase Diagrams

By the end of this section, you will be able to:

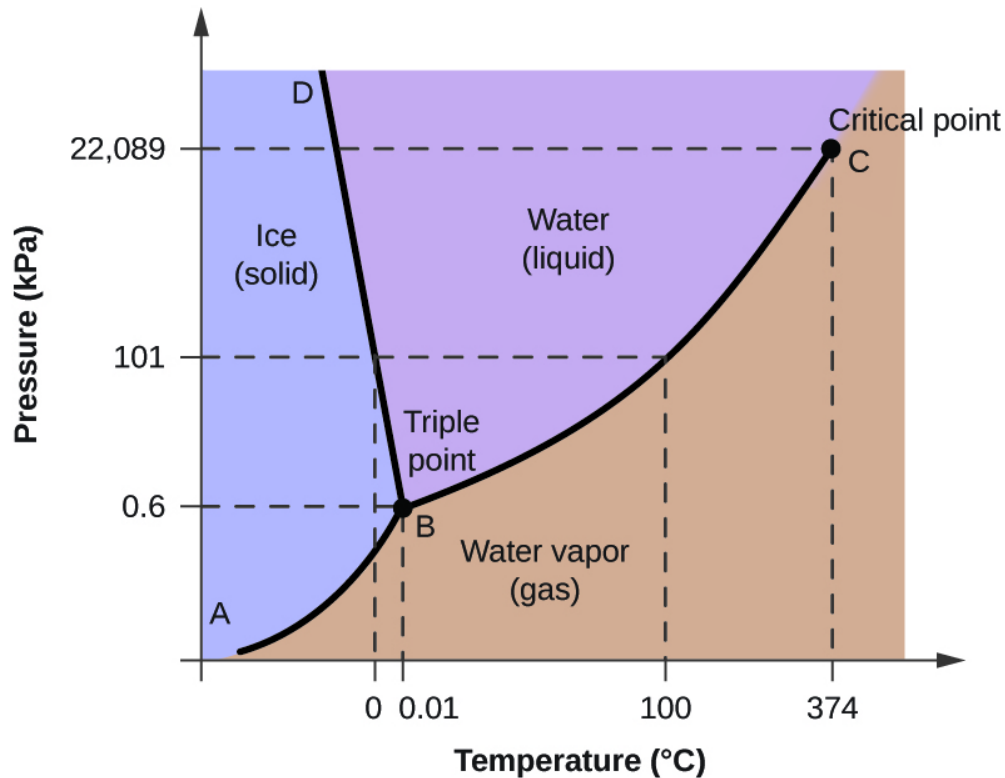
- Explain the construction and use of a typical phase diagram
- Use phase diagrams to identify stable phases at given temperatures and pressures, and to describe phase transitions resulting from changes in these properties
- Describe the supercritical fluid phase of matter

In the previous module, the variation of a liquid's equilibrium vapor pressure with temperature was described. Considering the definition of boiling point, plots of vapor pressure versus temperature represent how the boiling point of the liquid varies with pressure. Also described was the use of heating and cooling curves to determine a substance's melting (or freezing) point. Making such measurements over a wide range of pressures yields data that may be presented graphically as a phase diagram. A **phase diagram** combines plots of pressure versus temperature for the liquid-gas, solid-liquid, and solid-gas phase-transition equilibria of a substance. These diagrams indicate the physical states that exist under specific conditions of pressure and temperature, and also provide the pressure dependence of the phase-transition temperatures (melting points, sublimation points, boiling points). A typical phase diagram for a pure substance is shown in [\[link\]](#).



The physical state of a substance and its phase-transition temperatures are represented graphically in a phase diagram.

To illustrate the utility of these plots, consider the phase diagram for water shown in [\[link\]](#).



The pressure and temperature axes on this phase diagram of water are not drawn to constant scale in order to illustrate several important properties.

We can use the phase diagram to identify the physical state of a sample of water under specified conditions of pressure and temperature. For example, a pressure of 50 kPa and a temperature of -10°C correspond to the region of the diagram labeled “ice.” Under these conditions, water exists only as a solid (ice). A pressure of 50 kPa and a temperature of 50°C correspond to the “water” region—here, water exists only as a liquid. At 25 kPa and 200°C , water exists only in the gaseous state. Note that on the H_2O phase diagram, the pressure and temperature axes are not drawn to a constant scale in order to permit the illustration of several important features as described here.

The curve BC in [\[link\]](#) is the plot of vapor pressure versus temperature as described in the previous module of this chapter. This “liquid-vapor” curve

separates the liquid and gaseous regions of the phase diagram and provides the boiling point for water at any pressure. For example, at 1 atm, the boiling point is 100 °C. Notice that the liquid-vapor curve terminates at a temperature of 374 °C and a pressure of 218 atm, indicating that water cannot exist as a liquid above this temperature, regardless of the pressure. The physical properties of water under these conditions are intermediate between those of its liquid and gaseous phases. This unique state of matter is called a supercritical fluid, a topic that will be described in the next section of this module.

The solid-vapor curve, labeled AB in [\[link\]](#), indicates the temperatures and pressures at which ice and water vapor are in equilibrium. These temperature-pressure data pairs correspond to the sublimation, or deposition, points for water. If we could zoom in on the solid-gas line in [\[link\]](#), we would see that ice has a vapor pressure of about 0.20 kPa at −10 °C. Thus, if we place a frozen sample in a vacuum with a pressure less than 0.20 kPa, ice will sublime. This is the basis for the “freeze-drying” process often used to preserve foods, such as the ice cream shown in [\[link\]](#).



Freeze-dried foods, like this ice cream, are dehydrated by sublimation at pressures below the triple point for water. (credit: "lwao"/Flickr)

The solid-liquid curve labeled BD shows the temperatures and pressures at which ice and liquid water are in equilibrium, representing the melting/freezing points for water. Note that this curve exhibits a slight negative slope (greatly exaggerated for clarity), indicating that the melting point for water decreases slightly as pressure increases. Water is an unusual substance in this regard, as most substances exhibit an increase in melting point with increasing pressure. This behavior is partly responsible for the movement of glaciers, like the one shown in [\[link\]](#). The bottom of a glacier experiences an immense pressure due to its weight that can melt some of the ice, forming a layer of liquid water on which the glacier may more easily slide.



The immense pressures beneath glaciers result in partial melting to produce a layer of water that provides lubrication to assist glacial movement. This satellite photograph shows the advancing edge of the Perito Moreno glacier in Argentina. (credit: NASA)

The point of intersection of all three curves is labeled B in [\[link\]](#). At the pressure and temperature represented by this point, all three phases of water coexist in equilibrium. This temperature-pressure data pair is called the **triple point**. At pressures lower than the triple point, water cannot exist as a liquid, regardless of the temperature.

Example:

Determining the State of Water

Using the phase diagram for water given in [\[link\]](#), determine the state of water at the following temperatures and pressures:

- (a) $-10\text{ }^{\circ}\text{C}$ and 50 kPa
- (b) $25\text{ }^{\circ}\text{C}$ and 90 kPa
- (c) $50\text{ }^{\circ}\text{C}$ and 40 kPa
- (d) $80\text{ }^{\circ}\text{C}$ and 5 kPa
- (e) $-10\text{ }^{\circ}\text{C}$ and 0.3 kPa
- (f) $50\text{ }^{\circ}\text{C}$ and 0.3 kPa

Solution

Using the phase diagram for water, we can determine that the state of water at each temperature and pressure given are as follows: (a) solid; (b) liquid; (c) liquid; (d) gas; (e) solid; (f) gas.

Check Your Learning

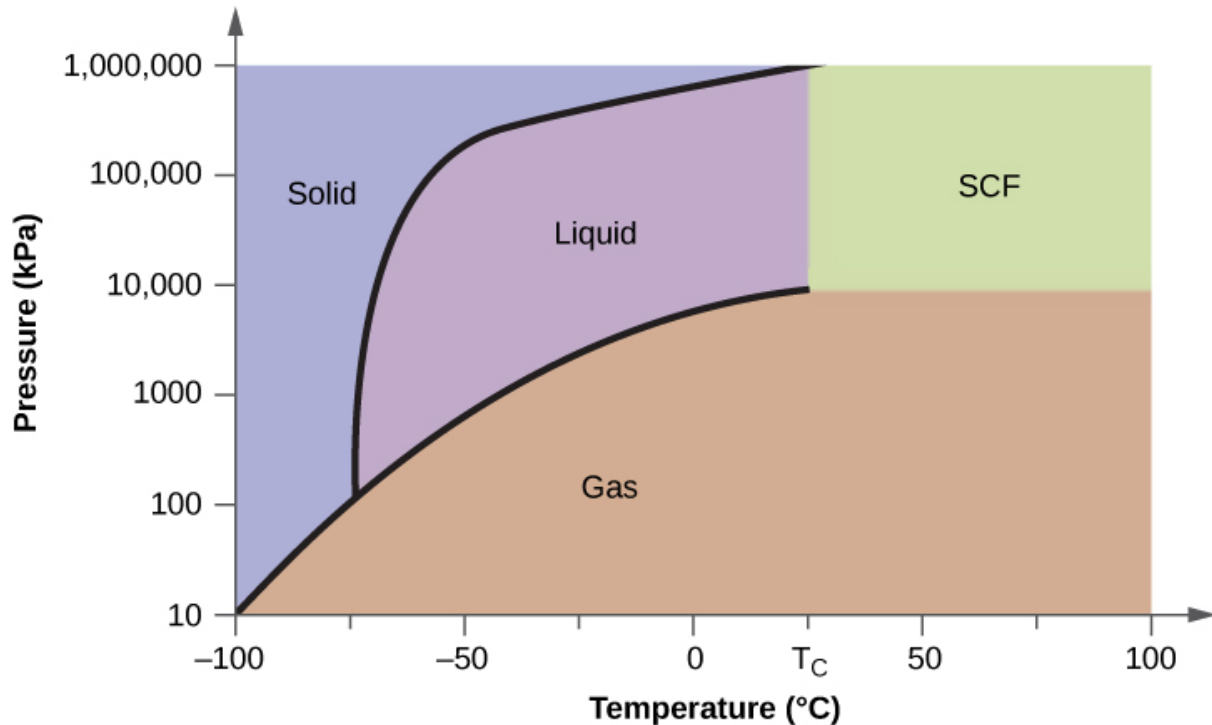
What phase changes can water undergo as the temperature changes if the pressure is held at 0.3 kPa? If the pressure is held at 50 kPa?

Note:

Answer:

At 0.3 kPa: $s \longrightarrow g$ at $-58\text{ }^{\circ}\text{C}$. At 50 kPa: $s \longrightarrow l$ at $0\text{ }^{\circ}\text{C}$, $l \longrightarrow g$ at $78\text{ }^{\circ}\text{C}$

Consider the phase diagram for carbon dioxide shown in [\[link\]](#) as another example. The solid-liquid curve exhibits a positive slope, indicating that the melting point for CO_2 increases with pressure as it does for most substances (water being a notable exception as described previously). Notice that the triple point is well above 1 atm, indicating that carbon dioxide cannot exist as a liquid under ambient pressure conditions. Instead, cooling gaseous carbon dioxide at 1 atm results in its deposition into the solid state. Likewise, solid carbon dioxide does not melt at 1 atm pressure but instead sublimates to yield gaseous CO_2 . Finally, notice that the critical point for carbon dioxide is observed at a relatively modest temperature and pressure in comparison to water.



The pressure and temperature axes on this phase diagram of carbon dioxide are not drawn to constant scale in order to illustrate several important properties.

Example:

Determining the State of Carbon Dioxide

Using the phase diagram for carbon dioxide shown in [\[link\]](#), determine the state of CO_2 at the following temperatures and pressures:

- (a) $-30\text{ }^\circ\text{C}$ and 2000 kPa
- (b) $-60\text{ }^\circ\text{C}$ and 1000 kPa
- (c) $-60\text{ }^\circ\text{C}$ and 100 kPa
- (d) $20\text{ }^\circ\text{C}$ and 1500 kPa
- (e) $0\text{ }^\circ\text{C}$ and 100 kPa
- (f) $20\text{ }^\circ\text{C}$ and 100 kPa

Solution

Using the phase diagram for carbon dioxide provided, we can determine that the state of CO₂ at each temperature and pressure given are as follows: (a) liquid; (b) solid; (c) gas; (d) liquid; (e) gas; (f) gas.

Check Your Learning

Determine the phase changes carbon dioxide undergoes when its temperature is varied, thus holding its pressure constant at 1500 kPa? At 500 kPa? At what approximate temperatures do these phase changes occur?

Note:

Answer:

at 1500 kPa: s \rightarrow l at $-45\text{ }^{\circ}\text{C}$, l \rightarrow g at $-10\text{ }^{\circ}\text{C}$;

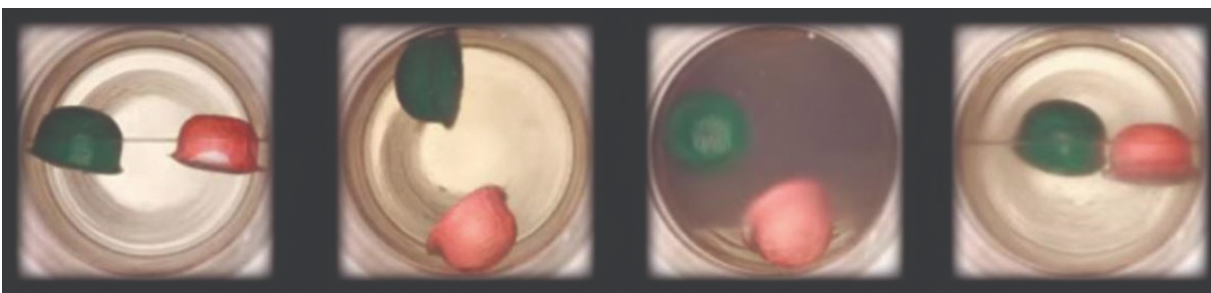
at 500 kPa: s \rightarrow g at $-58\text{ }^{\circ}\text{C}$

Supercritical Fluids

If we place a sample of water in a sealed container at $25\text{ }^{\circ}\text{C}$, remove the air, and let the vaporization-condensation equilibrium establish itself, we are left with a mixture of liquid water and water vapor at a pressure of 0.03 atm. A distinct boundary between the more dense liquid and the less dense gas is clearly observed. As we increase the temperature, the pressure of the water vapor increases, as described by the liquid-gas curve in the phase diagram for water ([\[link\]](#)), and a two-phase equilibrium of liquid and gaseous phases remains. At a temperature of $374\text{ }^{\circ}\text{C}$, the vapor pressure has risen to 218 atm, and any further increase in temperature results in the disappearance of the boundary between liquid and vapor phases. All of the water in the container is now present in a single phase whose physical properties are intermediate between those of the gaseous and liquid states. This phase of matter is called a **supercritical fluid**, and the temperature and pressure above which this phase exists is the **critical point** ([\[link\]](#)). Above its critical temperature, a gas cannot be liquefied no matter how much

pressure is applied. The pressure required to liquefy a gas at its critical temperature is called the critical pressure. The critical temperatures and critical pressures of some common substances are given in [\[link\]](#).

Substance	Critical Temperature (K)	Critical Pressure (atm)
hydrogen	33.2	12.8
nitrogen	126.0	33.5
oxygen	154.3	49.7
carbon dioxide	304.2	73.0
ammonia	405.5	111.5
sulfur dioxide	430.3	77.7
water	647.1	217.7



(a) A sealed container of liquid carbon dioxide slightly below its critical point is heated, resulting in (b) the formation of the supercritical fluid phase. Cooling the supercritical fluid lowers its temperature and pressure below the critical point, resulting in the reestablishment of separate liquid and gaseous phases (c and d). Colored floats illustrate differences in density between the liquid, gaseous, and supercritical fluid states. (credit: modification of work by “mrmrobin”/YouTube)

Note:



Observe the [liquid-to-supercritical fluid transition](#) for carbon dioxide.

Like a gas, a supercritical fluid will expand and fill a container, but its density is much greater than typical gas densities, typically being close to those for liquids. Similar to liquids, these fluids are capable of dissolving nonvolatile solutes. They exhibit essentially no surface tension and very low viscosities, however, so they can more effectively penetrate very small openings in a solid mixture and remove soluble components. These properties make supercritical fluids extremely useful solvents for a wide range of applications. For example, supercritical carbon dioxide has become a very popular solvent in the food industry, being used to decaffeinate coffee, remove fats from potato chips, and extract flavor and fragrance compounds from citrus oils. It is nontoxic, relatively inexpensive, and not

considered to be a pollutant. After use, the CO_2 can be easily recovered by reducing the pressure and collecting the resulting gas.

Example:

The Critical Temperature of Carbon Dioxide

If we shake a carbon dioxide fire extinguisher on a cool day ($18\text{ }^\circ\text{C}$), we can hear liquid CO_2 sloshing around inside the cylinder. However, the same cylinder appears to contain no liquid on a hot summer day ($35\text{ }^\circ\text{C}$). Explain these observations.

Solution

On the cool day, the temperature of the CO_2 is below the critical temperature of CO_2 , 304 K or $31\text{ }^\circ\text{C}$ ([link](#)), so liquid CO_2 is present in the cylinder. On the hot day, the temperature of the CO_2 is greater than its critical temperature of $31\text{ }^\circ\text{C}$. Above this temperature no amount of pressure can liquefy CO_2 so no liquid CO_2 exists in the fire extinguisher.

Check Your Learning

Ammonia can be liquefied by compression at room temperature; oxygen cannot be liquefied under these conditions. Why do the two gases exhibit different behavior?

Note:

Answer:

The critical temperature of ammonia is 405.5 K , which is higher than room temperature. The critical temperature of oxygen is below room temperature; thus oxygen cannot be liquefied at room temperature.

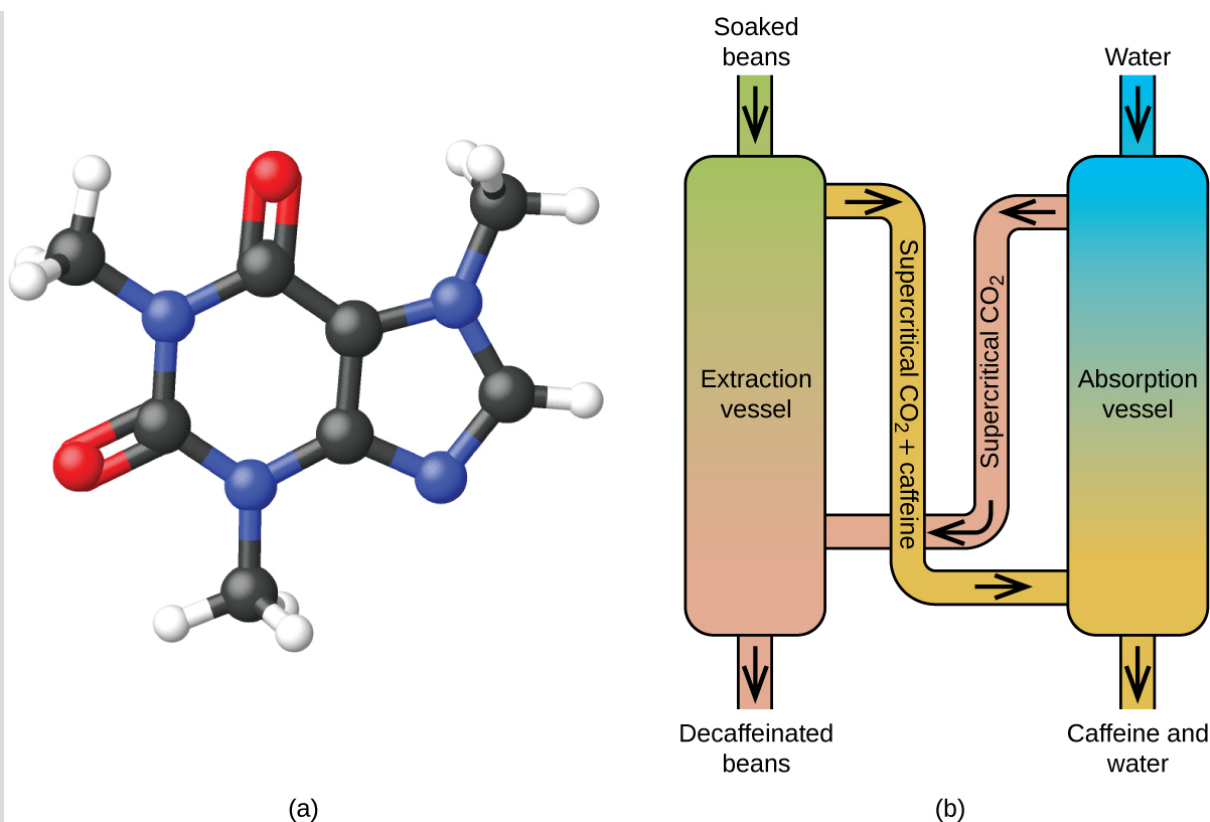
Note:

Decaffeinating Coffee Using Supercritical CO_2

Coffee is the world's second most widely traded commodity, following only petroleum. Across the globe, people love coffee's aroma and taste. Many of us also depend on one component of coffee—caffeine—to help us get going in the morning or stay alert in the afternoon. But late in the day, coffee's stimulant effect can keep you from sleeping, so you may choose to drink decaffeinated coffee in the evening.

Since the early 1900s, many methods have been used to decaffeinate coffee. All have advantages and disadvantages, and all depend on the physical and chemical properties of caffeine. Because caffeine is a somewhat polar molecule, it dissolves well in water, a polar liquid. However, since many of the other 400-plus compounds that contribute to coffee's taste and aroma also dissolve in H_2O , hot water decaffeination processes can also remove some of these compounds, adversely affecting the smell and taste of the decaffeinated coffee. Dichloromethane (CH_2Cl_2) and ethyl acetate ($\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$) have similar polarity to caffeine, and are therefore very effective solvents for caffeine extraction, but both also remove some flavor and aroma components, and their use requires long extraction and cleanup times. Because both of these solvents are toxic, health concerns have been raised regarding the effect of residual solvent remaining in the decaffeinated coffee.

Supercritical fluid extraction using carbon dioxide is now being widely used as a more effective and environmentally friendly decaffeination method ([\[link\]](#)). At temperatures above 304.2 K and pressures above 7376 kPa, CO_2 is a supercritical fluid, with properties of both gas and liquid. Like a gas, it penetrates deep into the coffee beans; like a liquid, it effectively dissolves certain substances. Supercritical carbon dioxide extraction of steamed coffee beans removes 97–99% of the caffeine, leaving coffee's flavor and aroma compounds intact. Because CO_2 is a gas under standard conditions, its removal from the extracted coffee beans is easily accomplished, as is the recovery of the caffeine from the extract. The caffeine recovered from coffee beans via this process is a valuable product that can be used subsequently as an additive to other foods or drugs.



(a) Caffeine molecules have both polar and nonpolar regions, making it soluble in solvents of varying polarities. (b) The schematic shows a typical decaffeination process involving supercritical carbon dioxide.

Key Concepts and Summary

The temperature and pressure conditions at which a substance exists in solid, liquid, and gaseous states are summarized in a phase diagram for that substance. Phase diagrams are combined plots of three pressure-temperature equilibrium curves: solid-liquid, liquid-gas, and solid-gas. These curves represent the relationships between phase-transition temperatures and pressures. The point of intersection of all three curves represents the substance's triple point—the temperature and pressure at which all three phases are in equilibrium. At pressures below the triple point, a substance

cannot exist in the liquid state, regardless of its temperature. The terminus of the liquid-gas curve represents the substance's critical point, the pressure and temperature above which a liquid phase cannot exist.

Chemistry End of Chapter Exercises

Exercise:

Problem:

From the phase diagram for water ([link](#)), determine the state of water at:

- (a) 35 °C and 85 kPa
- (b) -15 °C and 40 kPa
- (c) -15 °C and 0.1 kPa
- (d) 75 °C and 3 kPa
- (e) 40 °C and 0.1 kPa
- (f) 60 °C and 50 kPa

Exercise:

Problem:

What phase changes will take place when water is subjected to varying pressure at a constant temperature of 0.005 °C? At 40 °C? At -40 °C?

Solution:

At low pressures and 0.005 °C, the water is a gas. As the pressure increases to 4.6 torr, the water becomes a solid; as the pressure increases still more, it becomes a liquid. At 40 °C, water at low pressure is a vapor; at pressures higher than about 75 torr, it converts into a liquid. At -40 °C, water goes from a gas to a solid as the pressure increases above very low values.

Exercise:**Problem:**

Pressure cookers allow food to cook faster because the higher pressure inside the pressure cooker increases the boiling temperature of water. A particular pressure cooker has a safety valve that is set to vent steam if the pressure exceeds 3.4 atm. What is the approximate maximum temperature that can be reached inside this pressure cooker? Explain your reasoning.

Exercise:**Problem:**

From the phase diagram for carbon dioxide in [\[link\]](#), determine the state of CO₂ at:

- (a) 20 °C and 1000 kPa
- (b) 10 °C and 2000 kPa
- (c) 10 °C and 100 kPa
- (d) -40 °C and 500 kPa
- (e) -80 °C and 1500 kPa
- (f) -80 °C and 10 kPa

Solution:

(a) gas; (b) gas; (c) gas; (d) gas; (e) solid; (f) gas

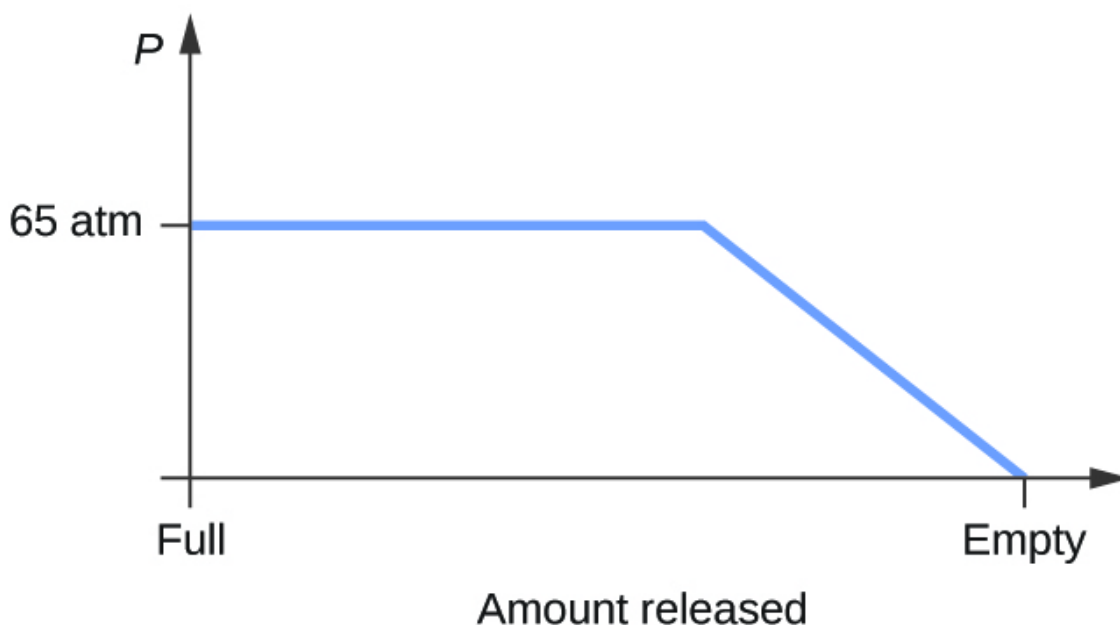
Exercise:

Problem:

Determine the phase changes that carbon dioxide undergoes as the pressure changes if the temperature is held at $-50\text{ }^{\circ}\text{C}$? If the temperature is held at $-40\text{ }^{\circ}\text{C}$? At $20\text{ }^{\circ}\text{C}$? (See the phase diagram in [\[link\]](#).)

Exercise:**Problem:**

Consider a cylinder containing a mixture of liquid carbon dioxide in equilibrium with gaseous carbon dioxide at an initial pressure of 65 atm and a temperature of $20\text{ }^{\circ}\text{C}$. Sketch a plot depicting the change in the cylinder pressure with time as gaseous carbon dioxide is released at constant temperature.

Solution:**Exercise:**

Problem:

Dry ice, $\text{CO}_2(\text{s})$, does not melt at atmospheric pressure. It sublimates at a temperature of $-78\text{ }^\circ\text{C}$. What is the lowest pressure at which $\text{CO}_2(\text{s})$ will melt to give $\text{CO}_2(\text{l})$? At approximately what temperature will this occur? (See [\[link\]](#) for the phase diagram.)

Exercise:**Problem:**

If a severe storm results in the loss of electricity, it may be necessary to use a clothesline to dry laundry. In many parts of the country in the dead of winter, the clothes will quickly freeze when they are hung on the line. If it does not snow, will they dry anyway? Explain your answer.

Solution:

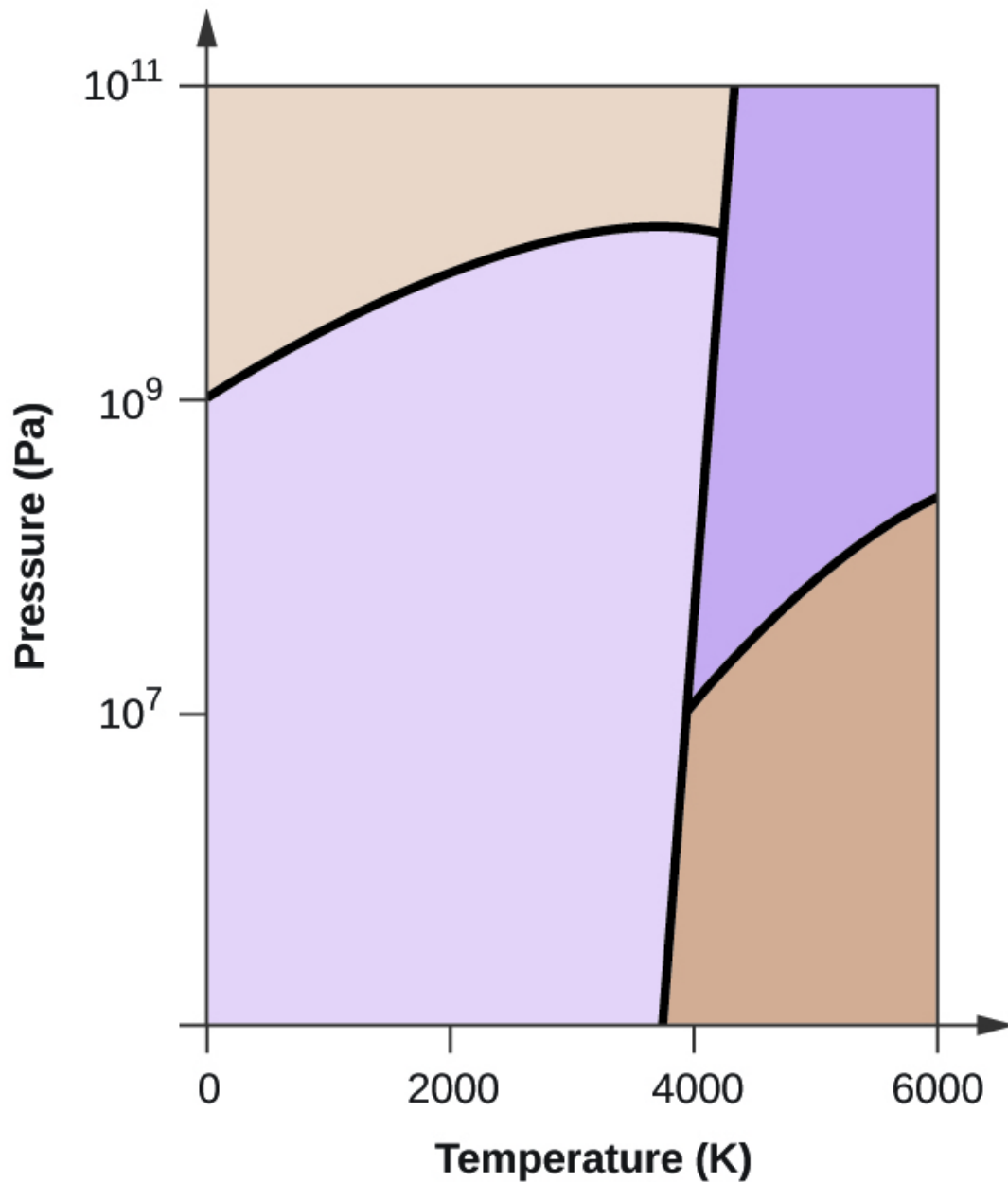
Yes, ice will sublime, although it may take it several days. Ice has a small vapor pressure, and some ice molecules form gas and escape from the ice crystals. As time passes, more and more solid converts to gas until eventually the clothes are dry.

Exercise:**Problem:**

Is it possible to liquefy nitrogen at room temperature (about $25\text{ }^\circ\text{C}$)? Is it possible to liquefy sulfur dioxide at room temperature? Explain your answers.

Exercise:**Problem:**

Elemental carbon has one gas phase, one liquid phase, and two different solid phases, as shown in the phase diagram:



- (a) On the phase diagram, label the gas and liquid regions.
- (b) Graphite is the most stable phase of carbon at normal conditions. On the phase diagram, label the graphite phase.
- (c) If graphite at normal conditions is heated to 2500 K while the pressure is increased to 10^{10} Pa, it is converted into diamond. Label the diamond phase.

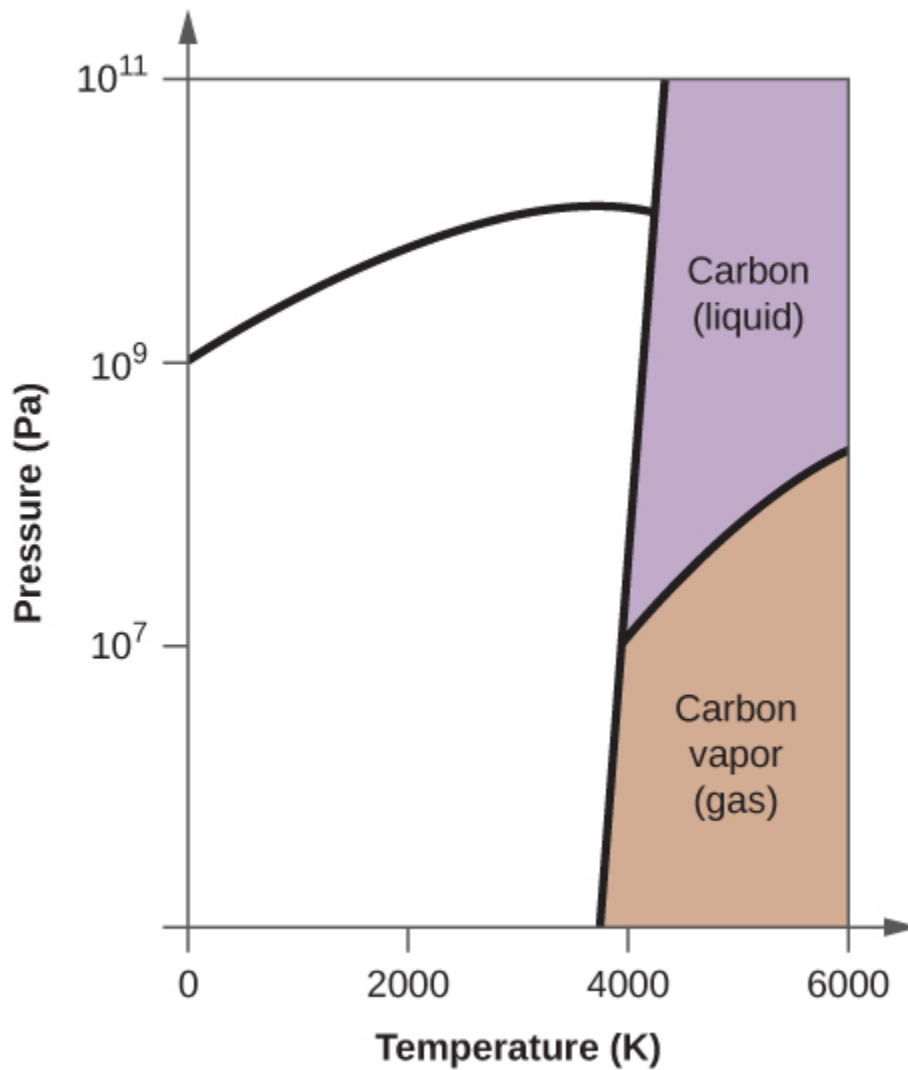
(d) Circle each triple point on the phase diagram.

(e) In what phase does carbon exist at 5000 K and 10^8 Pa?

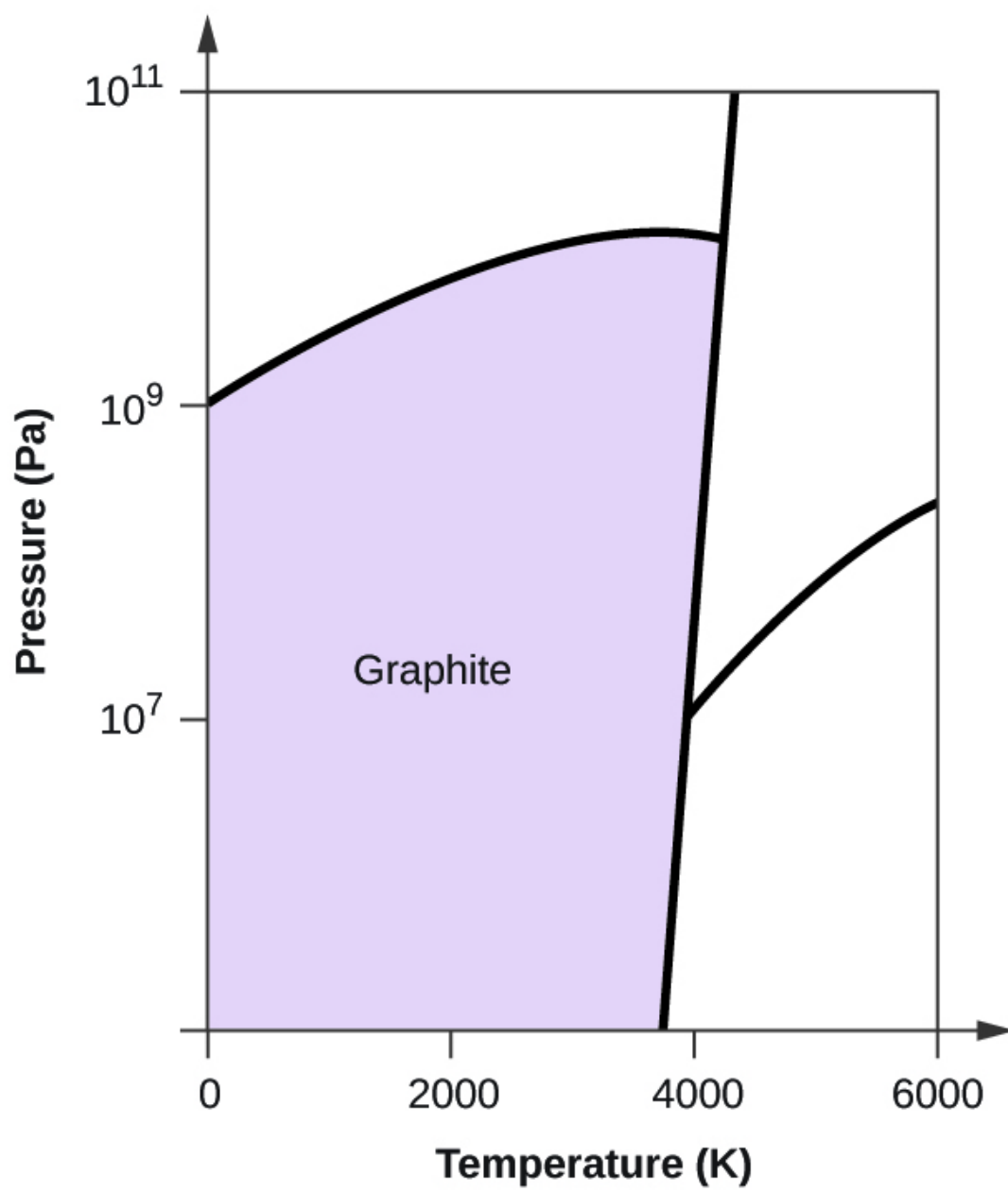
(f) If the temperature of a sample of carbon increases from 3000 K to 5000 K at a constant pressure of 10^6 Pa, which phase transition occurs, if any?

Solution:

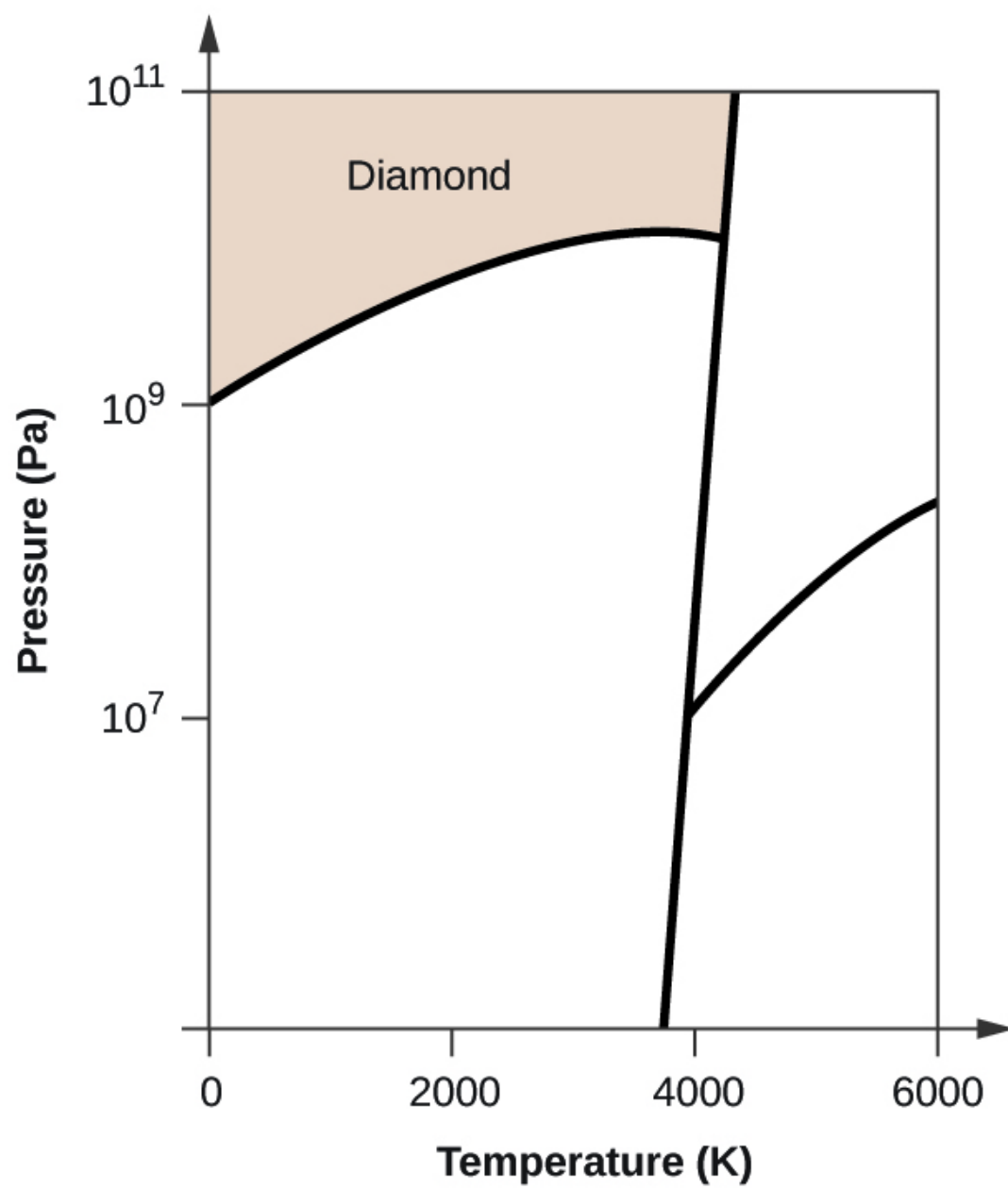
(a)



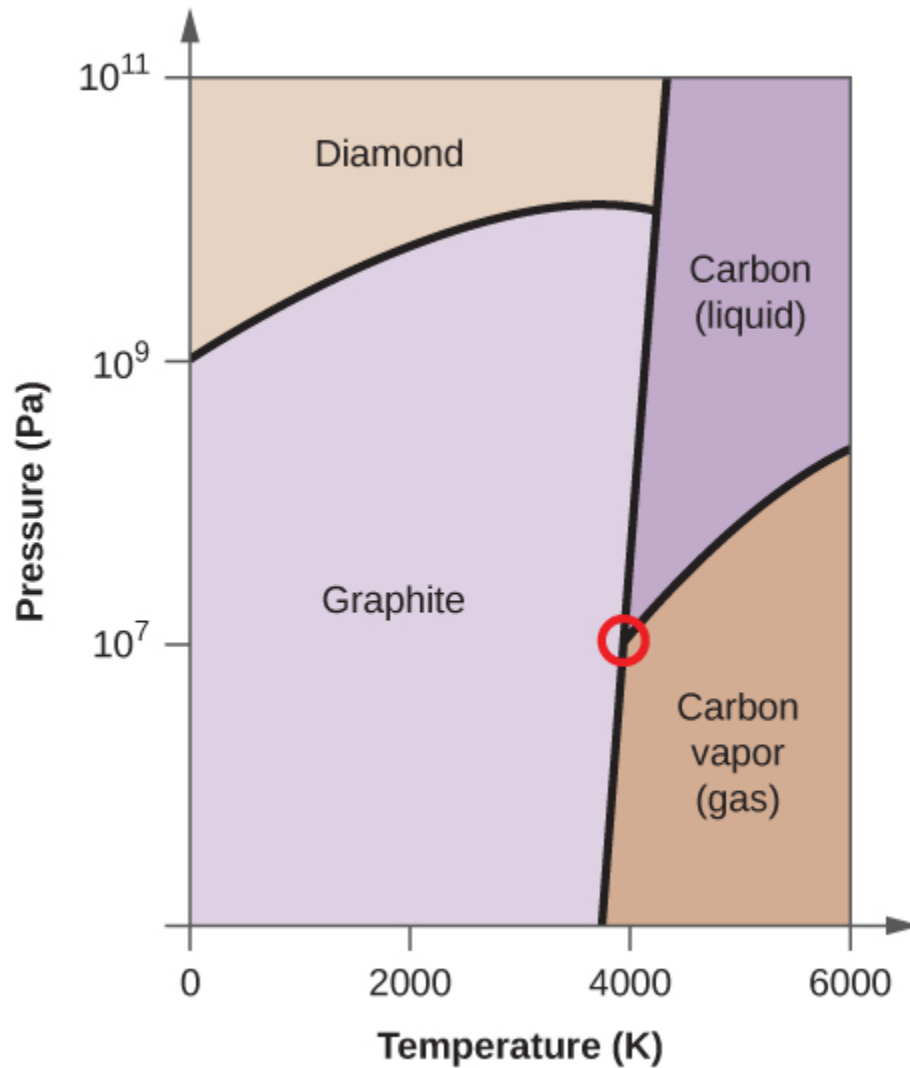
(b)



(c)



(d)



(e) liquid phase (f) sublimation

Glossary

critical point

temperature and pressure above which a gas cannot be condensed into a liquid

phase diagram

pressure-temperature graph summarizing conditions under which the phases of a substance can exist

supercritical fluid

substance at a temperature and pressure higher than its critical point; exhibits properties intermediate between those of gaseous and liquid states

triple point

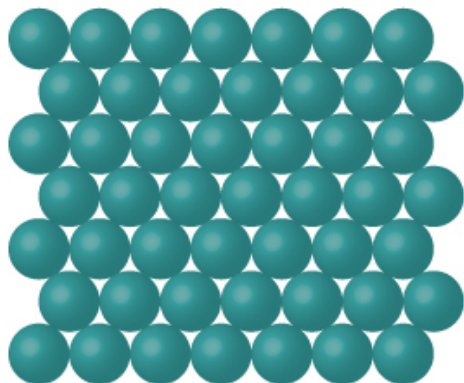
temperature and pressure at which the vapor, liquid, and solid phases of a substance are in equilibrium

The Solid State of Matter

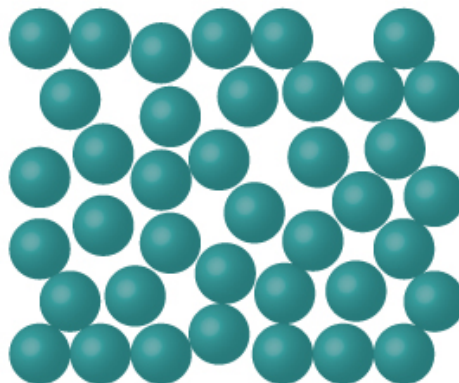
By the end of this section, you will be able to:

- Define and describe the bonding and properties of ionic, molecular, metallic, and covalent network crystalline solids
- Describe the main types of crystalline solids: ionic solids, metallic solids, covalent network solids, and molecular solids
- Explain the ways in which crystal defects can occur in a solid

When most liquids are cooled, they eventually freeze and form **crystalline solids**, solids in which the atoms, ions, or molecules are arranged in a definite repeating pattern. It is also possible for a liquid to freeze before its molecules become arranged in an orderly pattern. The resulting materials are called **amorphous solids** or noncrystalline solids (or, sometimes, glasses). The particles of such solids lack an ordered internal structure and are randomly arranged ([link](#)).



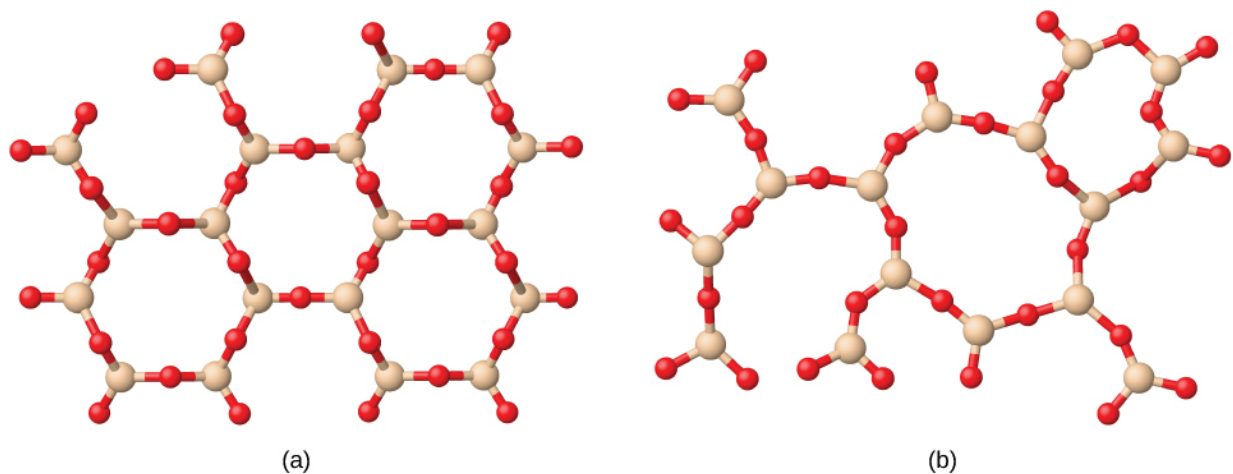
Crystalline



Amorphous

The entities of a solid phase may be arranged in a regular, repeating pattern (crystalline solids) or randomly (amorphous).

Metals and ionic compounds typically form ordered, crystalline solids. Substances that consist of large molecules, or a mixture of molecules whose movements are more restricted, often form amorphous solids. For examples, candle waxes are amorphous solids composed of large hydrocarbon molecules. Some substances, such as silicon dioxide (shown in [link](#)), can form either crystalline or amorphous solids, depending on the conditions under which it is produced. Also, amorphous solids may undergo a transition to the crystalline state under appropriate conditions.

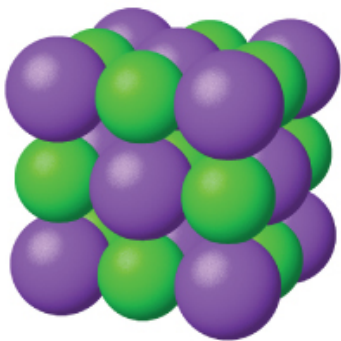


(a) Silicon dioxide, SiO_2 , is abundant in nature as one of several crystalline forms of the mineral quartz. (b) Rapid cooling of molten SiO_2 yields an amorphous solid known as “fused silica”.

Crystalline solids are generally classified according to the nature of the forces that hold its particles together. These forces are primarily responsible for the physical properties exhibited by the bulk solids. The following sections provide descriptions of the major types of crystalline solids: ionic, metallic, covalent network, and molecular.

Ionic Solids

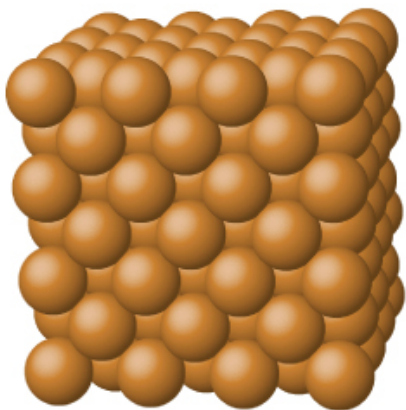
Ionic solids, such as sodium chloride and nickel oxide, are composed of positive and negative ions that are held together by electrostatic attractions, which can be quite strong ([link](#)). Many ionic crystals also have high melting points. This is due to the very strong attractions between the ions—in ionic compounds, the attractions between full charges are (much) larger than those between the partial charges in polar molecular compounds. This will be looked at in more detail in a later discussion of lattice energies. Although they are hard, they also tend to be brittle, and they shatter rather than bend. Ionic solids do not conduct electricity; however, they do conduct when molten or dissolved because their ions are free to move. Many simple compounds formed by the reaction of a metallic element with a nonmetallic element are ionic.



Sodium chloride is an ionic solid.

Metallic Solids

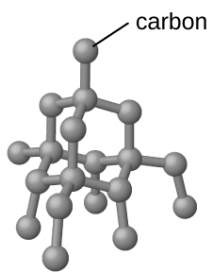
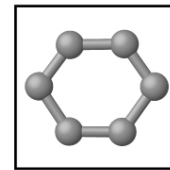
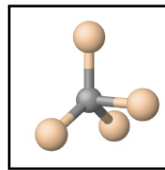
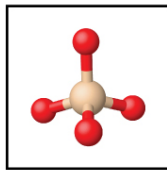
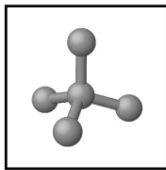
Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms [\[link\]](#). The structure of metallic crystals is often described as a uniform distribution of atomic nuclei within a “sea” of delocalized electrons. The atoms within such a metallic solid are held together by a unique force known as *metallic bonding* that gives rise to many useful and varied bulk properties. All exhibit high thermal and electrical conductivity, metallic luster, and malleability. Many are very hard and quite strong. Because of their malleability (the ability to deform under pressure or hammering), they do not shatter and, therefore, make useful construction materials. The melting points of the metals vary widely. Mercury is a liquid at room temperature, and the alkali metals melt below 200 °C. Several post-transition metals also have low melting points, whereas the transition metals melt at temperatures above 1000 °C. These differences reflect differences in strengths of metallic bonding among the metals.



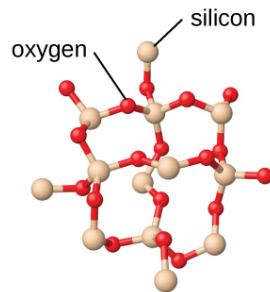
Copper is a metallic solid.

Covalent Network Solid

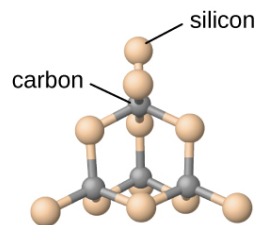
Covalent network solids include crystals of diamond, silicon, some other nonmetals, and some covalent compounds such as silicon dioxide (sand) and silicon carbide (carborundum, the abrasive on sandpaper). Many minerals have networks of covalent bonds. The atoms in these solids are held together by a network of covalent bonds, as shown in [\[link\]](#). To break or to melt a covalent network solid, covalent bonds must be broken. Because covalent bonds are relatively strong, covalent network solids are typically characterized by hardness, strength, and high melting points. For example, diamond is one of the hardest substances known and melts above 3500 °C.



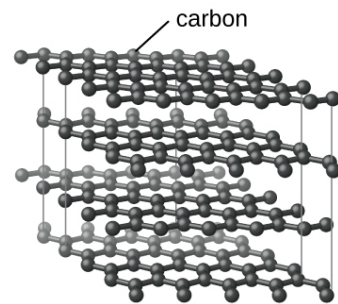
diamond



silicon dioxide



silicon carbide

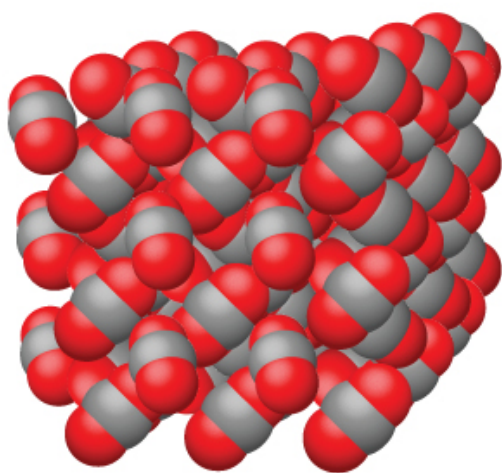


graphite

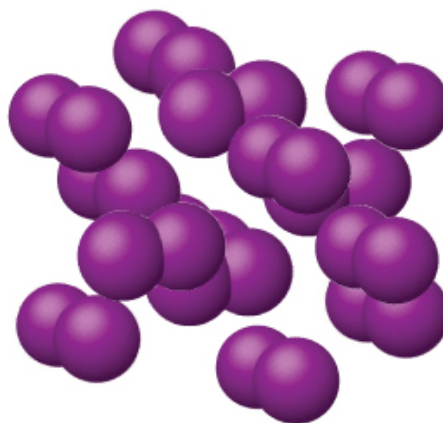
A covalent crystal contains a three-dimensional network of covalent bonds, as illustrated by the structures of diamond, silicon dioxide, silicon carbide, and graphite. Graphite is an exceptional example, composed of planar sheets of covalent crystals that are held together in layers by noncovalent forces. Unlike typical covalent solids, graphite is very soft and electrically conductive.

Molecular Solid

Molecular solids, such as ice, sucrose (table sugar), and iodine, as shown in [\[link\]](#), are composed of neutral molecules. The strengths of the attractive forces between the units present in different crystals vary widely, as indicated by the melting points of the crystals. Small symmetrical molecules (nonpolar molecules), such as H_2 , N_2 , O_2 , and F_2 , have weak attractive forces and form molecular solids with very low melting points (below $-200\text{ }^\circ\text{C}$). Substances consisting of larger, nonpolar molecules have larger attractive forces and melt at higher temperatures. Molecular solids composed of molecules with permanent dipole moments (polar molecules) melt at still higher temperatures. Examples include ice (melting point, $0\text{ }^\circ\text{C}$) and table sugar (melting point, $185\text{ }^\circ\text{C}$).



carbon dioxide



iodine

Carbon dioxide (CO_2) consists of small, nonpolar molecules and forms a molecular solid with a melting point of $-78\text{ }^\circ\text{C}$. Iodine (I_2) consists of larger, nonpolar molecules and forms a molecular solid that melts at $114\text{ }^\circ\text{C}$.

Properties of Solids

A crystalline solid, like those listed in [\[link\]](#), has a precise melting temperature because each atom or molecule of the same type is held in place with the same forces or energy. Thus, the attractions between the units that make up the crystal all have the same strength and all require the same amount of energy to be broken. The gradual softening of an amorphous material differs dramatically from the distinct melting of a crystalline solid. This results from the structural nonequivalence of the molecules in the amorphous

solid. Some forces are weaker than others, and when an amorphous material is heated, the weakest intermolecular attractions break first. As the temperature is increased further, the stronger attractions are broken. Thus amorphous materials soften over a range of temperatures.

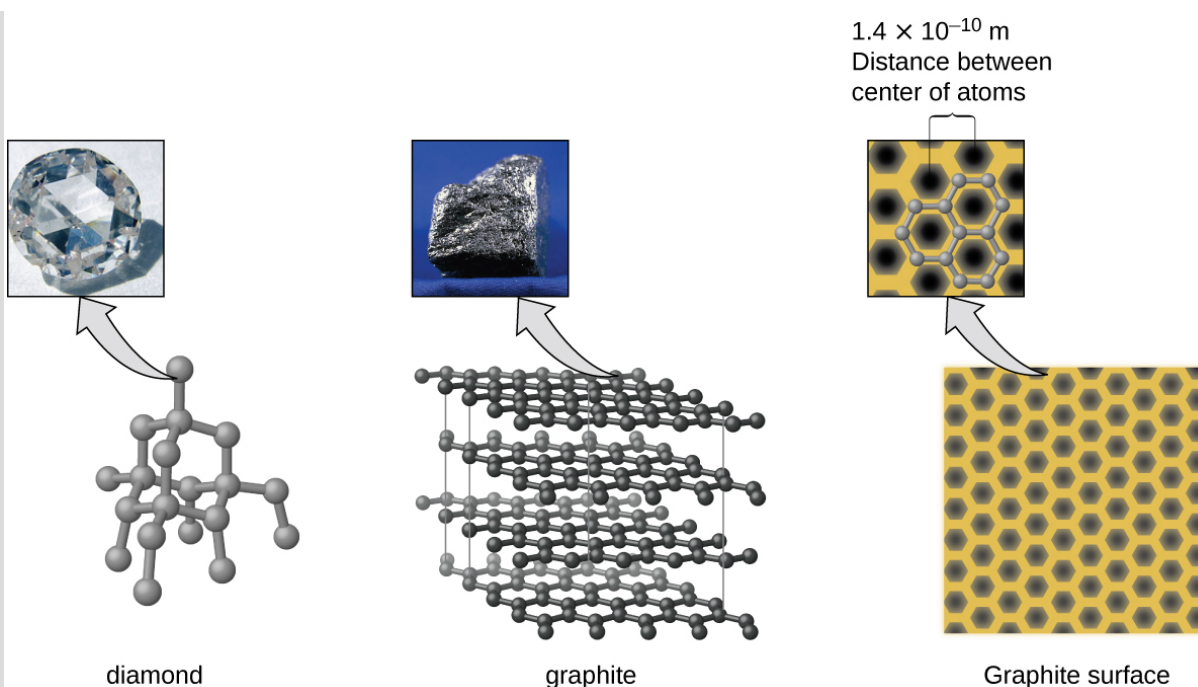
Types of Crystalline Solids and Their Properties				
Type of Solid	Type of Particles	Type of Attractions	Properties	Examples
ionic	ions	ionic bonds	hard, brittle, conducts electricity as a liquid but not as a solid, high to very high melting points	NaCl, Al ₂ O ₃
metallic	atoms of electropositive elements	metallic bonds	shiny, malleable, ductile, conducts heat and electricity well, variable hardness and melting temperature	Cu, Fe, Ti, Pb, U
covalent network	atoms of electronegative elements	covalent bonds	very hard, not conductive, very high melting points	C (diamond), SiO ₂ , SiC

Types of Crystalline Solids and Their Properties				
Type of Solid	Type of Particles	Type of Attractions	Properties	Examples
molecular	molecules (or atoms)	IMFs	variable hardness, variable brittleness, not conductive, low melting points	H ₂ O, CO ₂ , I ₂ , C ₁₂ H ₂₂ O ₁₁

Note:

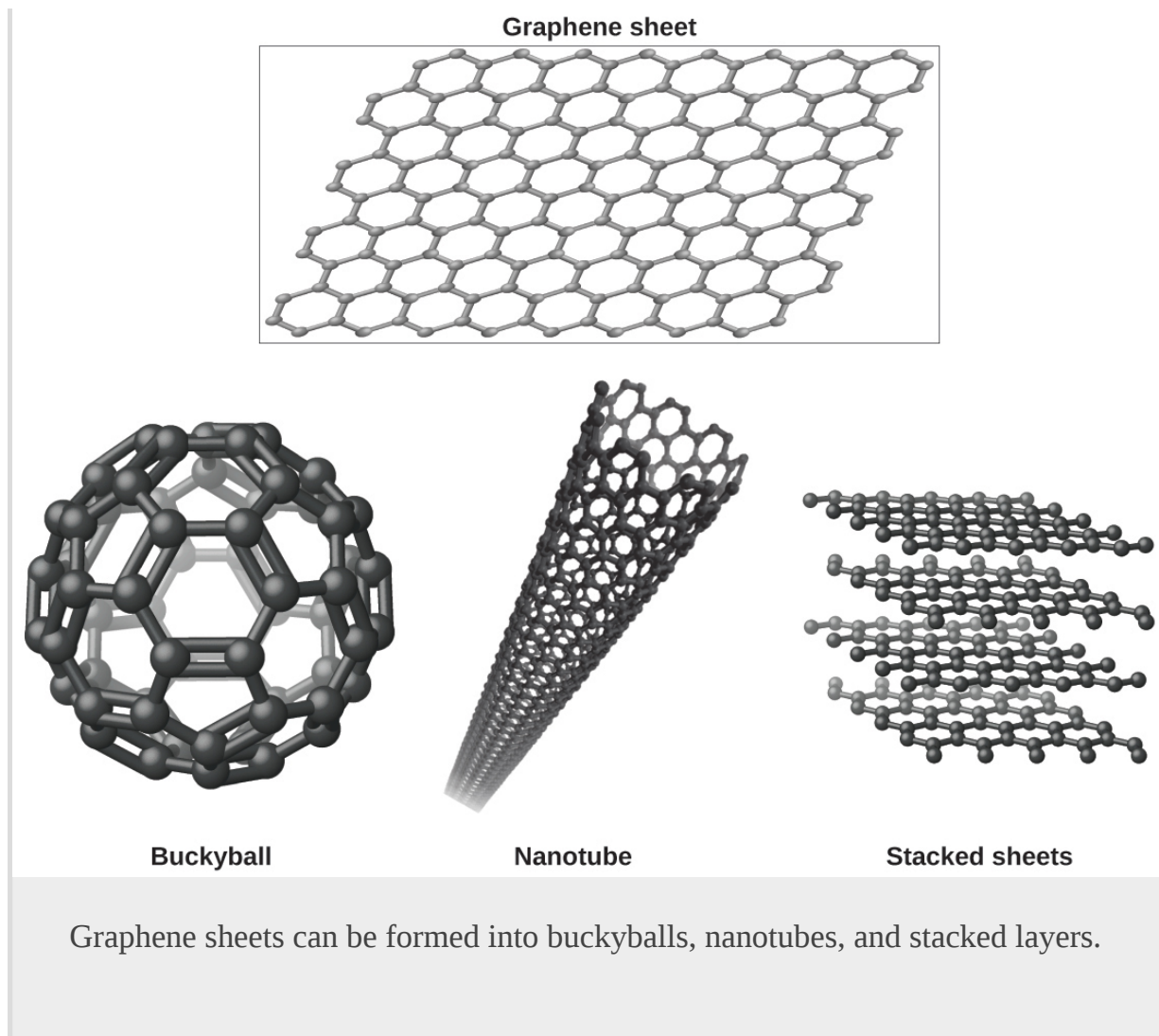
Graphene: Material of the Future

Carbon is an essential element in our world. The unique properties of carbon atoms allow the existence of carbon-based life forms such as ourselves. Carbon forms a huge variety of substances that we use on a daily basis, including those shown in [\[link\]](#). You may be familiar with diamond and graphite, the two most common *allotropes* of carbon. (Allotropes are different structural forms of the same element.) Diamond is one of the hardest-known substances, whereas graphite is soft enough to be used as pencil lead. These very different properties stem from the different arrangements of the carbon atoms in the different allotropes.



Diamond is extremely hard because of the strong bonding between carbon atoms in all directions. Graphite (in pencil lead) rubs off onto paper due to the weak attractions between the carbon layers. An image of a graphite surface shows the distance between the centers of adjacent carbon atoms. (credit left photo: modification of work by Steve Jurvetson; credit middle photo: modification of work by United States Geological Survey)

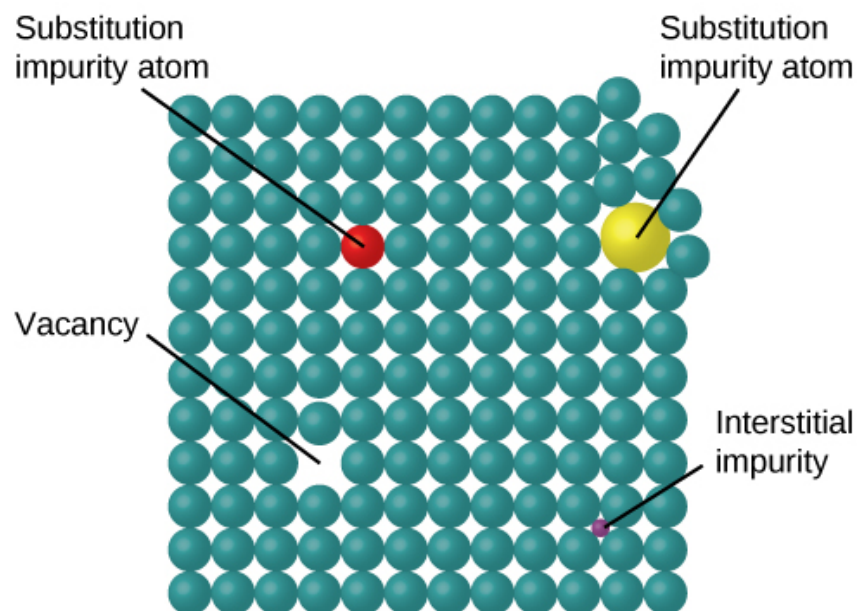
You may be less familiar with a recently discovered form of carbon: graphene. Graphene was first isolated in 2004 by using tape to peel off thinner and thinner layers from graphite. It is essentially a single sheet (one atom thick) of graphite. Graphene, illustrated in [\[link\]](#), is not only strong and lightweight, but it is also an excellent conductor of electricity and heat. These properties may prove very useful in a wide range of applications, such as vastly improved computer chips and circuits, better batteries and solar cells, and stronger and lighter structural materials. The 2010 Nobel Prize in Physics was awarded to Andre Geim and Konstantin Novoselov for their pioneering work with graphene.



Crystal Defects

In a crystalline solid, the atoms, ions, or molecules are arranged in a definite repeating pattern, but occasional defects may occur in the pattern. Several types of defects are known, as illustrated in [\[link\]](#). **Vacancies** are defects that occur when positions that should contain atoms or ions are vacant. Less commonly, some atoms or ions in a crystal may occupy positions, called **interstitial sites**, located between the regular positions for atoms. Other distortions are found in impure crystals, as, for example, when the cations, anions, or molecules of the impurity are too large to fit into the regular positions without distorting the structure. Trace amounts of impurities are sometimes added to a crystal (a process known as *doping*) in order to create defects in the structure that yield desirable changes in its properties. For example, silicon crystals

are doped with varying amounts of different elements to yield suitable electrical properties for their use in the manufacture of semiconductors and computer chips.



Types of crystal defects include vacancies, interstitial atoms, and substitutions impurities.

Key Concepts and Summary

Some substances form crystalline solids consisting of particles in a very organized structure; others form amorphous (noncrystalline) solids with an internal structure that is not ordered. The main types of crystalline solids are ionic solids, metallic solids, covalent network solids, and molecular solids. The properties of the different kinds of crystalline solids are due to the types of particles of which they consist, the arrangements of the particles, and the strengths of the attractions between them. Because their particles experience identical attractions, crystalline solids have distinct melting temperatures; the particles in amorphous solids experience a range of interactions, so they soften gradually and melt over a range of temperatures. Some crystalline solids have defects in the definite repeating pattern of their particles. These defects (which include vacancies, atoms or ions not in the regular positions, and impurities) change physical properties such as electrical conductivity, which is exploited in the silicon crystals used to manufacture computer chips.

Chemistry End of Chapter Exercises

Exercise:

Problem: What types of liquids typically form amorphous solids?

Exercise:

Problem:

At very low temperatures oxygen, O_2 , freezes and forms a crystalline solid. Which best describes these crystals?

- (a) ionic
 - (b) covalent network
 - (c) metallic
 - (d) amorphous
 - (e) molecular crystals
-

Solution:

- (e) molecular crystals

Exercise:

Problem:

As it cools, olive oil slowly solidifies and forms a solid over a range of temperatures. Which best describes the solid?

- (a) ionic
- (b) covalent network
- (c) metallic
- (d) amorphous
- (e) molecular crystals

Exercise:

Problem:

Explain why ice, which is a crystalline solid, has a melting temperature of $0\text{ }^{\circ}\text{C}$, whereas butter, which is an amorphous solid, softens over a range of temperatures.

Solution:

Ice has a crystalline structure stabilized by hydrogen bonding. These intermolecular forces are of comparable strength and thus require the same amount of energy to overcome. As a result, ice melts at a single temperature and not over a range of temperatures. The various, very large molecules that compose butter experience varied van der Waals attractions of various strengths that are overcome at various temperatures, and so the melting process occurs over a wide temperature range.

Exercise:**Problem:**

Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:

- (a) SiO_2
- (b) KCl
- (c) Cu
- (d) CO_2
- (e) C (diamond)
- (f) BaSO_4
- (g) NH_3
- (h) NH_4F
- (i) $\text{C}_2\text{H}_5\text{OH}$

Exercise:**Problem:**

Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:

- (a) CaCl_2
- (b) SiC
- (c) N_2
- (d) Fe
- (e) C (graphite)
- (f) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
- (g) HCl
- (h) NH_4NO_3
- (i) K_3PO_4

Solution:

(a) ionic; (b) covalent network; (c) molecular; (d) metallic; (e) covalent network;
 (f) molecular; (g) molecular; (h) ionic; (i) ionic

Exercise:

Problem:

Classify each substance in the table as either a metallic, ionic, molecular, or covalent network solid:

Substance	Appearance	Melting Point	Electrical Conductivity	Solubility in Water
X	lustrous, malleable	1500 °C	high	insoluble
Y	soft, yellow	113 °C	none	insoluble
Z	hard, white	800 °C	only if melted/dissolved	soluble

Exercise:**Problem:**

Classify each substance in the table as either a metallic, ionic, molecular, or covalent network solid:

Substance	Appearance	Melting Point	Electrical Conductivity	Solubility in Water
X	brittle, white	800 °C	only if melted/dissolved	soluble
Y	shiny, malleable	1100 °C	high	insoluble
Z	hard, colorless	3550 °C	none	insoluble

Solution:

X = ionic; Y = metallic; Z = covalent network

Exercise:**Problem:**

Identify the following substances as ionic, metallic, covalent network, or molecular solids:

Substance A is malleable, ductile, conducts electricity well, and has a melting point of 1135 °C. Substance B is brittle, does not conduct electricity as a solid but does when molten, and has a melting point of 2072 °C. Substance C is very hard, does not conduct electricity, and has a melting point of 3440 °C. Substance D is soft, does not conduct electricity, and has a melting point of 185 °C.

Exercise:

Problem:

Substance A is shiny, conducts electricity well, and melts at 975 °C. Substance A is likely a(n):

- (a) ionic solid
 - (b) metallic solid
 - (c) molecular solid
 - (d) covalent network solid
-

Solution:

- (b) metallic solid

Exercise:**Problem:**

Substance B is hard, does not conduct electricity, and melts at 1200 °C. Substance B is likely a(n):

- (a) ionic solid
- (b) metallic solid
- (c) molecular solid
- (d) covalent network solid

Glossary

amorphous solid

(also, noncrystalline solid) solid in which the particles lack an ordered internal structure

covalent network solid

solid whose particles are held together by covalent bonds

crystalline solid

solid in which the particles are arranged in a definite repeating pattern

interstitial sites

spaces between the regular particle positions in any array of atoms or ions

ionic solid

solid composed of positive and negative ions held together by strong electrostatic attractions

metallic solid

solid composed of metal atoms

molecular solid

solid composed of neutral molecules held together by intermolecular forces of attraction

vacancy

defect that occurs when a position that should contain an atom or ion is vacant

Lattice Structures in Crystalline Solids

By the end of this section, you will be able to:

- Describe the arrangement of atoms and ions in crystalline structures
- Compute ionic radii using unit cell dimensions
- Explain the use of X-ray diffraction measurements in determining crystalline structures

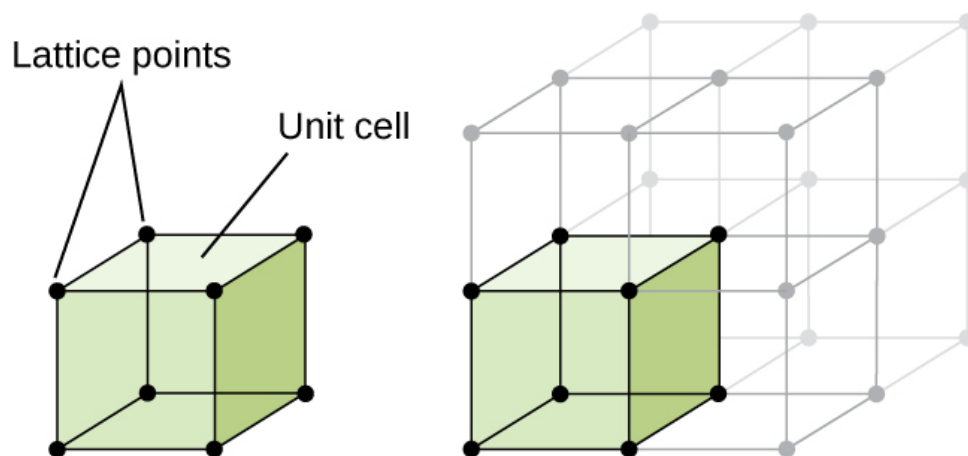
Over 90% of naturally occurring and man-made solids are crystalline. Most solids form with a regular arrangement of their particles because the overall attractive interactions between particles are maximized, and the total intermolecular energy is minimized, when the particles pack in the most efficient manner. The regular arrangement at an atomic level is often reflected at a macroscopic level. In this module, we will explore some of the details about the structures of metallic and ionic crystalline solids, and learn how these structures are determined experimentally.

The Structures of Metals

We will begin our discussion of crystalline solids by considering elemental metals, which are relatively simple because each contains only one type of atom. A pure metal is a crystalline solid with metal atoms packed closely together in a repeating pattern. Some of the properties of metals in general, such as their malleability and ductility, are largely due to having identical atoms arranged in a regular pattern. The different properties of one metal compared to another partially depend on the sizes of their atoms and the specifics of their spatial arrangements. We will explore the similarities and differences of four of the most common metal crystal geometries in the sections that follow.

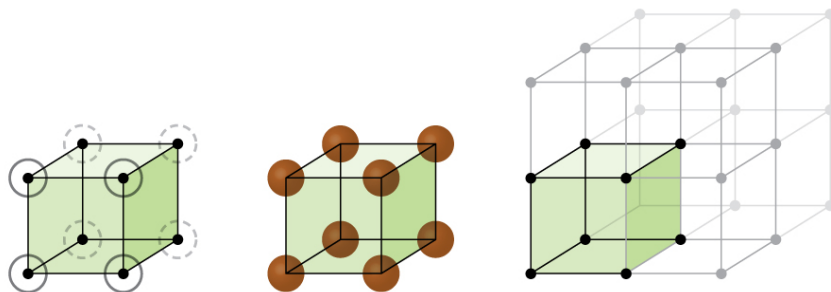
Unit Cells of Metals

The structure of a crystalline solid, whether a metal or not, is best described by considering its simplest repeating unit, which is referred to as its **unit cell**. The unit cell consists of lattice points that represent the locations of atoms or ions. The entire structure then consists of this unit cell repeating in three dimensions, as illustrated in [\[link\]](#).



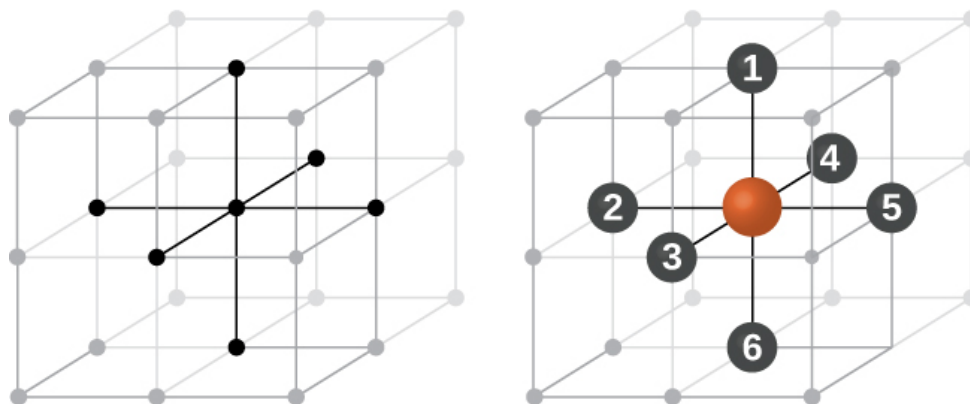
A unit cell shows the locations of lattice points repeating in all directions.

Let us begin our investigation of crystal lattice structure and unit cells with the most straightforward structure and the most basic unit cell. To visualize this, imagine taking a large number of identical spheres, such as tennis balls, and arranging them uniformly in a container. The simplest way to do this would be to make layers in which the spheres in one layer are directly above those in the layer below, as illustrated in [\[link\]](#). This arrangement is called **simple cubic structure**, and the unit cell is called the **simple cubic unit cell** or primitive cubic unit cell.



When metal atoms are arranged with spheres in one layer directly above or below spheres in another layer, the lattice structure is called simple cubic. Note that the spheres are in contact.

In a simple cubic structure, the spheres are not packed as closely as they could be, and they only “fill” about 52% of the volume of the container. This is a relatively inefficient arrangement, and only one metal (polonium, Po) crystallizes in a simple cubic structure. As shown in [\[link\]](#), a solid with this type of arrangement consists of planes (or layers) in which each atom contacts only the four nearest neighbors in its layer; one atom directly above it in the layer above; and one atom directly below it in the layer below. The number of other particles that each particle in a crystalline solid contacts is known as its **coordination number**. For a polonium atom in a simple cubic array, the coordination number is, therefore, six.

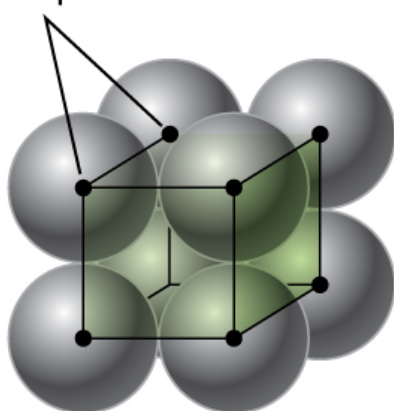


An atom in a simple cubic lattice structure contacts six other atoms, so it

has a coordination number of six.

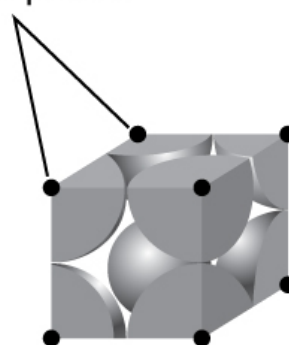
In a simple cubic lattice, the unit cell that repeats in all directions is a cube defined by the centers of eight atoms, as shown in [\[link\]](#). Atoms at adjacent corners of this unit cell contact each other, so the edge length of this cell is equal to two atomic radii, or one atomic diameter. A cubic unit cell contains only the parts of these atoms that are within it. Since an atom at a corner of a simple cubic unit cell is contained by a total of eight unit cells, only one-eighth of that atom is within a specific unit cell. And since each simple cubic unit cell has one atom at each of its eight “corners,” there is $8 \times \frac{1}{8} = 1$ atom within one simple cubic unit cell.

Lattice points



Simple cubic lattice cell

Lattice points



8 corners

A simple cubic lattice unit cell contains one-eighth of an atom at each of its eight corners, so it contains one atom total.

Example:

Calculation of Atomic Radius and Density for Metals, Part 1

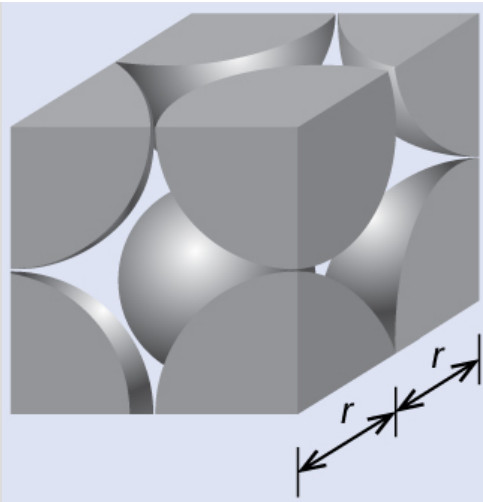
The edge length of the unit cell of alpha polonium is 336 pm.

(a) Determine the radius of a polonium atom.

(b) Determine the density of alpha polonium.

Solution

Alpha polonium crystallizes in a simple cubic unit cell:



(a) Two adjacent Po atoms contact each other, so the edge length of this cell is equal to two Po atomic radii: $l = 2r$. Therefore, the radius of Po is $r = \frac{l}{2} = \frac{336 \text{ pm}}{2} = 168 \text{ pm}$.

(b) Density is given by $\text{density} = \frac{\text{mass}}{\text{volume}}$. The density of polonium can be found by determining the density of its unit cell (the mass contained within a unit cell divided by the volume of the unit cell). Since a Po unit cell contains one-eighth of a Po atom at each of its eight corners, a unit cell contains one Po atom.

The mass of a Po unit cell can be found by:

Equation:

$$1 \text{ Po unit cell} \times \frac{1 \text{ Po atom}}{1 \text{ Po unit cell}} \times \frac{1 \text{ mol Po}}{6.022 \times 10^{23} \text{ Po atoms}} \times \frac{208.998 \text{ g}}{1 \text{ mol Po}} = 3.47 \times 10^{-22} \text{ g}$$

The volume of a Po unit cell can be found by:

Equation:

$$V = l^3 = (336 \times 10^{-10} \text{ cm})^3 = 3.79 \times 10^{-23} \text{ cm}^3$$

(Note that the edge length was converted from pm to cm to get the usual volume units for density.)

Therefore, the density of Po = $\frac{3.471 \times 10^{-22} \text{ g}}{3.79 \times 10^{-23} \text{ cm}^3} = 9.16 \text{ g/cm}^3$

Check Your Learning

The edge length of the unit cell for nickel is 0.3524 nm. The density of Ni is 8.90 g/cm^3 . Does nickel crystallize in a simple cubic structure? Explain.

Note:

Answer:

No. If Ni was simple cubic, its density would be given by:

$$1 \text{ Ni atom} \times \frac{1 \text{ mol Ni}}{6.022 \times 10^{23} \text{ Ni atoms}} \times \frac{58.693 \text{ g}}{1 \text{ mol Ni}} = 9.746 \times 10^{-23} \text{ g}$$

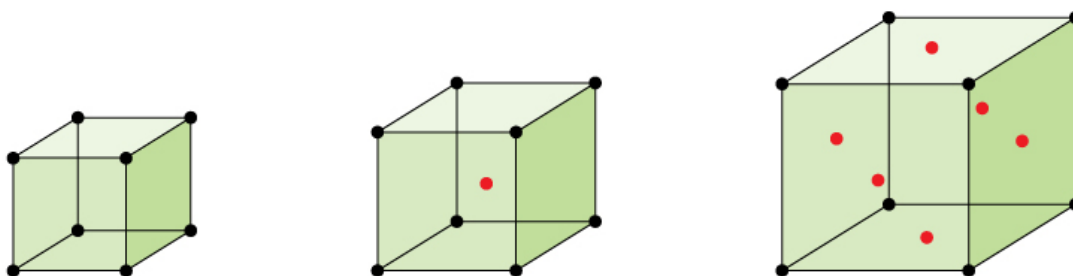
$$V = l^3 = (3.524 \times 10^{-8} \text{ cm})^3 = 4.376 \times 10^{-23} \text{ cm}^3$$

$$\text{Then the density of Ni would be} = \frac{9.746 \times 10^{-23} \text{ g}}{4.376 \times 10^{-23} \text{ cm}^3} = 2.23 \text{ g/cm}^3$$

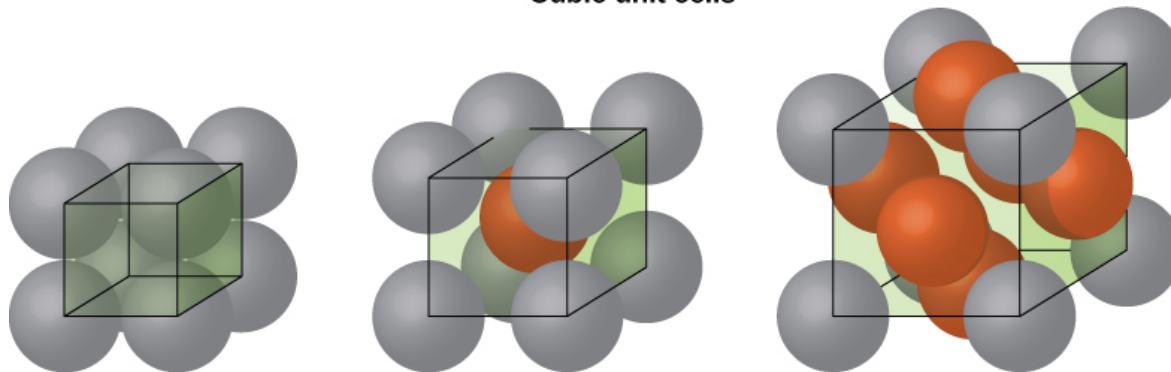
Since the actual density of Ni is not close to this, Ni does not form a simple cubic structure.

Most metal crystals are one of the four major types of unit cells. For now, we will focus on the three cubic unit cells: simple cubic (which we have already seen), **body-centered cubic unit cell**, and **face-centered cubic unit cell**—all of which are illustrated in [\[link\]](#). (Note that there are actually seven different lattice systems, some of which have more than one type of lattice, for a total of 14 different types of unit cells. We leave the more complicated geometries for later in this module.)

Lattice point locations



Cubic unit cells



Simple cubic

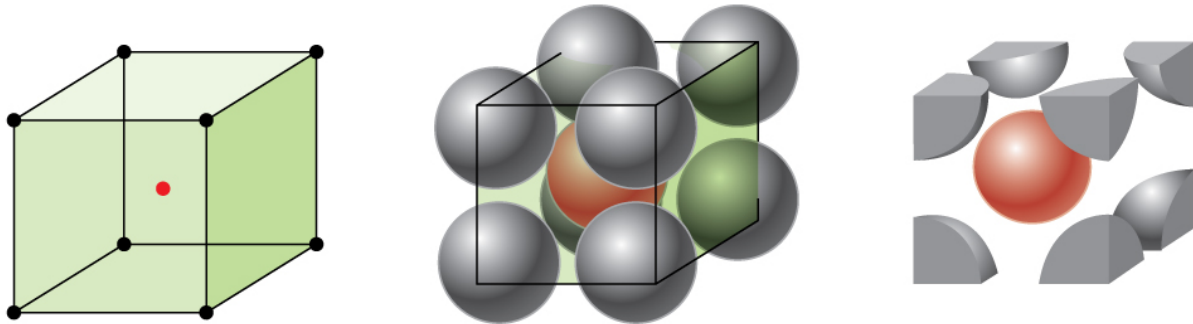
Body-centered cubic

Face-centered cubic

Cubic unit cells of metals show (in the upper figures) the locations of lattice points and (in the lower figures) metal atoms located in the unit cell.

Some metals crystallize in an arrangement that has a cubic unit cell with atoms at all of the corners and an atom in the center, as shown in [\[link\]](#). This is called a **body-centered cubic (BCC) solid**. Atoms in the corners of a BCC unit cell do not contact each other but contact the atom in the center. A BCC unit cell contains two atoms: one-eighth of an atom at each of the eight corners ($8 \times \frac{1}{8} = 1$ atom from the corners) plus one atom from the center. Any atom in this structure touches four atoms

in the layer above it and four atoms in the layer below it. Thus, an atom in a BCC structure has a coordination number of eight.

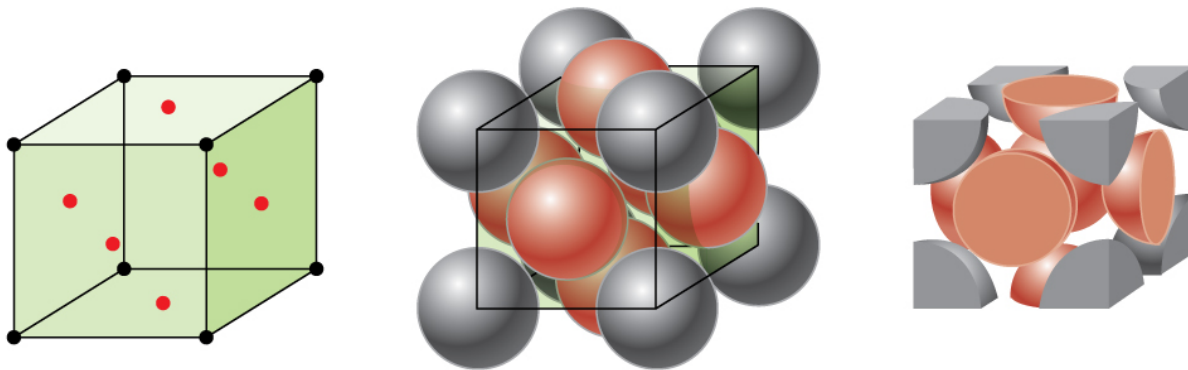


Body-centered cubic structure

In a body-centered cubic structure, atoms in a specific layer do not touch each other. Each atom touches four atoms in the layer above it and four atoms in the layer below it.

Atoms in BCC arrangements are much more efficiently packed than in a simple cubic structure, occupying about 68% of the total volume. Isomorphous metals with a BCC structure include K, Ba, Cr, Mo, W, and Fe at room temperature. (Elements or compounds that crystallize with the same structure are said to be **isomorphous**.)

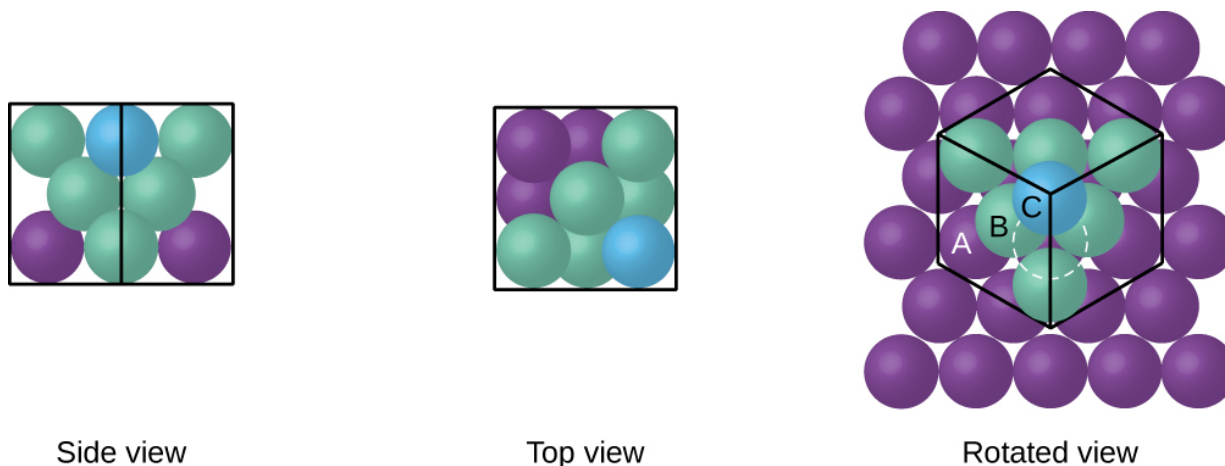
Many other metals, such as aluminum, copper, and lead, crystallize in an arrangement that has a cubic unit cell with atoms at all of the corners and at the centers of each face, as illustrated in [\[link\]](#). This arrangement is called a **face-centered cubic (FCC) solid**. A FCC unit cell contains four atoms: one-eighth of an atom at each of the eight corners ($8 \times \frac{1}{8} = 1$ atom from the corners) and one-half of an atom on each of the six faces ($6 \times \frac{1}{2} = 3$ atoms from the faces). The atoms at the corners touch the atoms in the centers of the adjacent faces along the face diagonals of the cube. Because the atoms are on identical lattice points, they have identical environments.



Face-centered cubic structure

A face-centered cubic solid has atoms at the corners and, as the name implies, at the centers of the faces of its unit cells.

Atoms in an FCC arrangement are packed as closely together as possible, with atoms occupying 74% of the volume. This structure is also called **cubic closest packing (CCP)**. In CCP, there are three repeating layers of hexagonally arranged atoms. Each atom contacts six atoms in its own layer, three in the layer above, and three in the layer below. In this arrangement, each atom touches 12 near neighbors, and therefore has a coordination number of 12. The fact that FCC and CCP arrangements are equivalent may not be immediately obvious, but why they are actually the same structure is illustrated in [\[link\]](#).



Side view

Top view

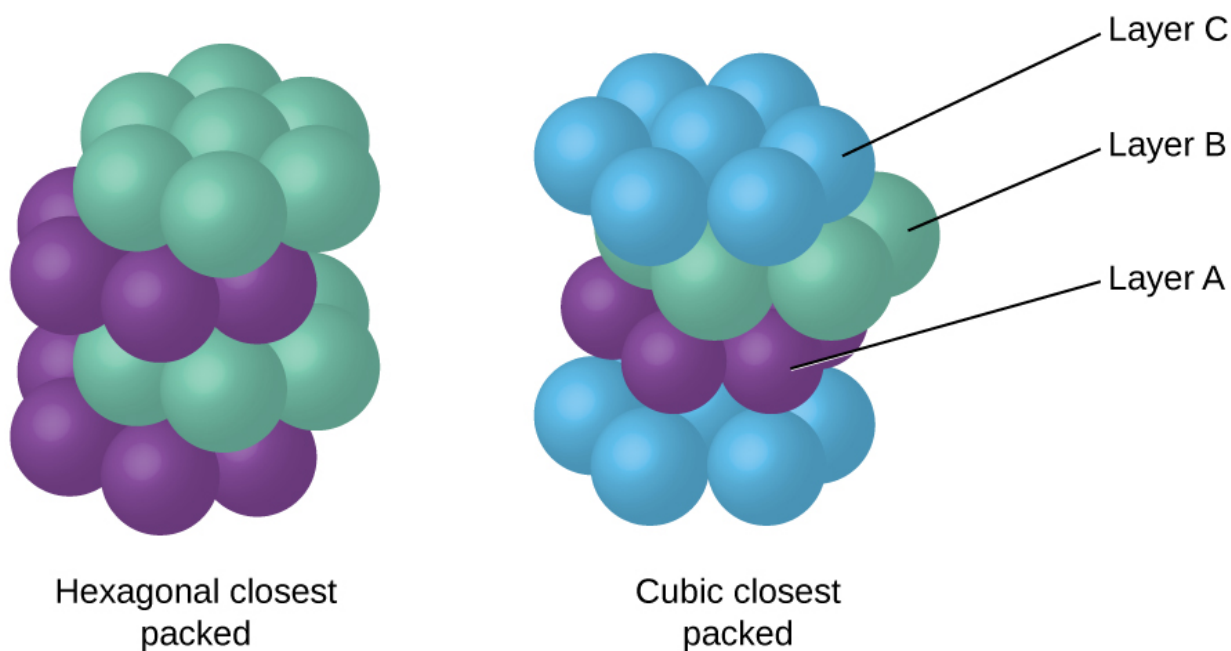
Rotated view

Cubic closest packed structure

A CCP arrangement consists of three repeating layers (ABCABC...) of hexagonally arranged atoms. Atoms in a CCP structure have a coordination number of 12 because they contact six atoms in their layer, plus three atoms in the layer above and three atoms in the layer below. By rotating our perspective, we can see that a CCP structure has a unit cell with a face containing an atom from layer A at one corner, atoms from layer B across a diagonal (at two corners and in the

middle of the face), and an atom from layer C at the remaining corner. This is the same as a face-centered cubic arrangement.

Because closer packing maximizes the overall attractions between atoms and minimizes the total intermolecular energy, the atoms in most metals pack in this manner. We find two types of closest packing in simple metallic crystalline structures: CCP, which we have already encountered, and **hexagonal closest packing (HCP)** shown in [\[link\]](#). Both consist of repeating layers of hexagonally arranged atoms. In both types, a second layer (B) is placed on the first layer (A) so that each atom in the second layer is in contact with three atoms in the first layer. The third layer is positioned in one of two ways. In HCP, atoms in the third layer are directly above atoms in the first layer (i.e., the third layer is also type A), and the stacking consists of alternating type A and type B close-packed layers (i.e., ABABAB...). In CCP, atoms in the third layer are not above atoms in either of the first two layers (i.e., the third layer is type C), and the stacking consists of alternating type A, type B, and type C close-packed layers (i.e., ABCABCABC...). About two-thirds of all metals crystallize in closest-packed arrays with coordination numbers of 12. Metals that crystallize in an HCP structure include Cd, Co, Li, Mg, Na, and Zn, and metals that crystallize in a CCP structure include Ag, Al, Ca, Cu, Ni, Pb, and Pt.



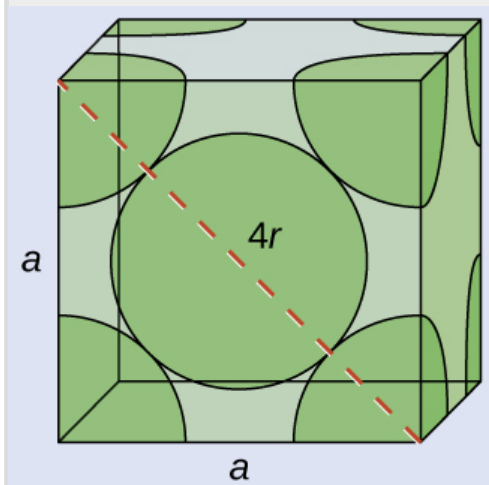
In both types of closest packing, atoms are packed as compactly as possible. Hexagonal closest packing consists of two alternating layers (ABABAB...). Cubic closest packing consists of three alternating layers (ABCABCABC...).

Example:**Calculation of Atomic Radius and Density for Metals, Part 2**

Calcium crystallizes in a face-centered cubic structure. The edge length of its unit cell is 558.8 pm.

(a) What is the atomic radius of Ca in this structure?

(b) Calculate the density of Ca.

Solution

(a) In an FCC structure, Ca atoms contact each other across the diagonal of the face, so the length of the diagonal is equal to four Ca atomic radii ($d = 4r$). Two adjacent edges and the diagonal of the face form a right triangle, with the length of each side equal to 558.8 pm and the length of the hypotenuse equal to four Ca atomic radii:

Equation:

$$a^2 + a^2 = d^2 \rightarrow (558.8 \text{ pm})^2 + (558.8 \text{ pm})^2 = (4r)^2$$

Solving this gives $r = \sqrt{\frac{(558.8 \text{ pm})^2 + (558.8 \text{ pm})^2}{16}} = 197.6 \text{ pm}$ for a Ca radius.

(b) Density is given by $\text{density} = \frac{\text{mass}}{\text{volume}}$. The density of calcium can be found by determining the density of its unit cell: for example, the mass contained within a unit cell divided by the volume of the unit cell. A face-centered Ca unit cell has one-eighth of an atom at each of the eight corners ($8 \times \frac{1}{8} = 1 \text{ atom}$) and one-half of an atom on each of the six faces ($6 \times \frac{1}{2} = 3 \text{ atoms}$), for a total of four atoms in the unit cell.

The mass of the unit cell can be found by:

Equation:

$$1 \text{ Ca unit cell} \times \frac{4 \text{ Ca atoms}}{1 \text{ Ca unit cell}} \times \frac{1 \text{ mol Ca}}{6.022 \times 10^{23} \text{ Ca atoms}} \times \frac{40.078 \text{ g}}{1 \text{ mol Ca}} = 2.662 \times 10^{-22} \text{ g}$$

The volume of a Ca unit cell can be found by:

Equation:

$$V = a^3 = (558.8 \times 10^{-10} \text{ cm})^3 = 1.745 \times 10^{-22} \text{ cm}^3$$

(Note that the edge length was converted from pm to cm to get the usual volume units for density.)

Then, the density of Ca = $\frac{2.662 \times 10^{-22} \text{ g}}{1.745 \times 10^{-22} \text{ cm}^3} = 1.53 \text{ g/cm}^3$

Check Your Learning

Silver crystallizes in an FCC structure. The edge length of its unit cell is 409 pm.

(a) What is the atomic radius of Ag in this structure?

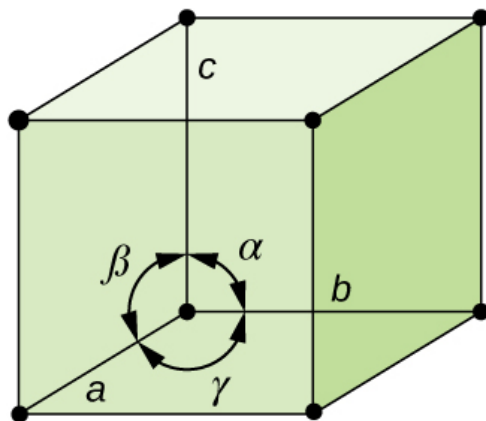
(b) Calculate the density of Ag.

Note:

Answer:

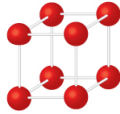
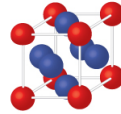
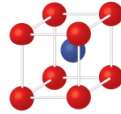
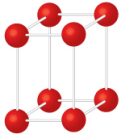
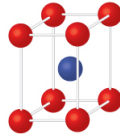
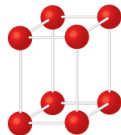
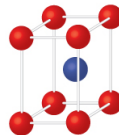
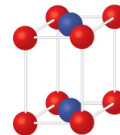
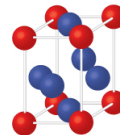
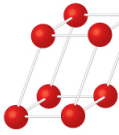
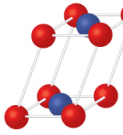
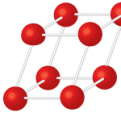
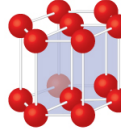
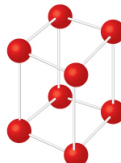
(a) 144 pm; (b) 10.5 g/cm³

In general, a unit cell is defined by the lengths of three axes (a , b , and c) and the angles (α , β , and γ) between them, as illustrated in [\[link\]](#). The axes are defined as being the lengths between points in the space lattice. Consequently, unit cell axes join points with identical environments.



A unit cell is defined by the lengths of its three axes (a , b , and c) and the angles (α , β , and γ) between the axes.

There are seven different lattice systems, some of which have more than one type of lattice, for a total of fourteen different unit cells, which have the shapes shown in [\[link\]](#).

System/Axes/Angles	Unit Cells			
Cubic $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$				
	Simple	Face-centered	Body-centered	
Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$				
	Simple	Body-centered		
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$				
	Simple	Body-centered	Base-centered	Face-centered
Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$				
	Simple	Base-centered		
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$				
Hexagonal $a = b \neq c$ $\alpha = \beta = 90^\circ; \gamma = 120^\circ$				
Rhombohedral $a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$				

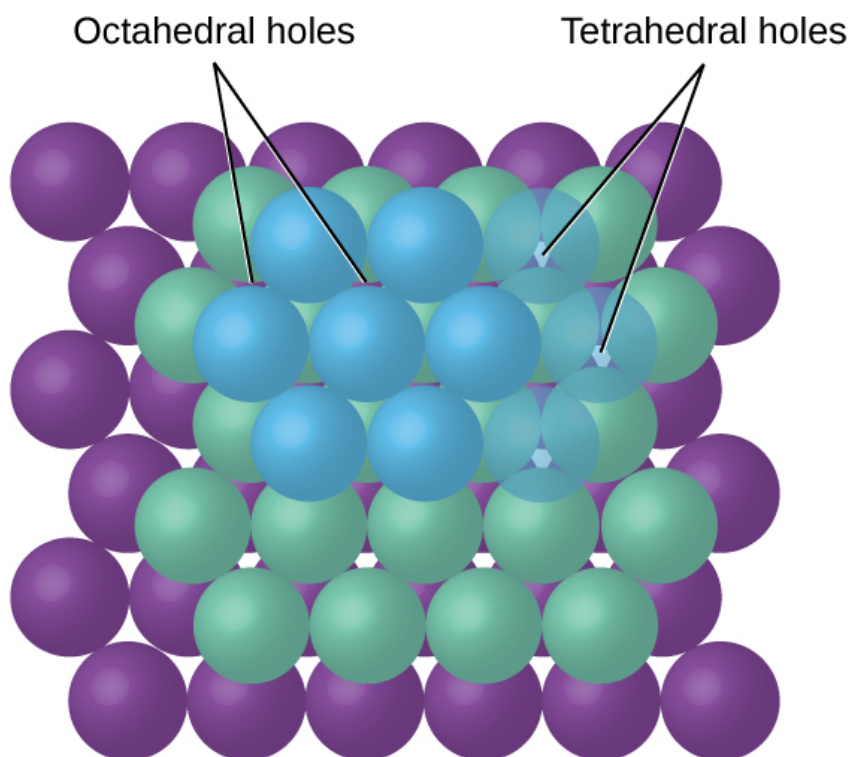
There are seven different lattice systems and 14 different unit cells.

The Structures of Ionic Crystals

Ionic crystals consist of two or more different kinds of ions that usually have different sizes. The packing of these ions into a crystal structure is more complex than the packing of metal atoms that are the same size.

Most monatomic ions behave as charged spheres, and their attraction for ions of opposite charge is the same in every direction. Consequently, stable structures for ionic compounds result (1) when ions of one charge are surrounded by as many ions as possible of the opposite charge and (2) when the cations and anions are in contact with each other. Structures are determined by two principal factors: the relative sizes of the ions and the ratio of the numbers of positive and negative ions in the compound.

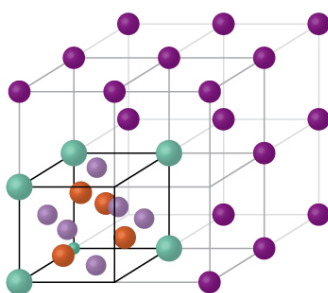
In simple ionic structures, we usually find the anions, which are normally larger than the cations, arranged in a closest-packed array. (As seen previously, additional electrons attracted to the same nucleus make anions larger and fewer electrons attracted to the same nucleus make cations smaller when compared to the atoms from which they are formed.) The smaller cations commonly occupy one of two types of **holes** (or interstices) remaining between the anions. The smaller of the holes is found between three anions in one plane and one anion in an adjacent plane. The four anions surrounding this hole are arranged at the corners of a tetrahedron, so the hole is called a **tetrahedral hole**. The larger type of hole is found at the center of six anions (three in one layer and three in an adjacent layer) located at the corners of an octahedron; this is called an **octahedral hole**. [\[link\]](#) illustrates both of these types of holes.



Cations may occupy two types of holes between anions: octahedral holes or tetrahedral holes.

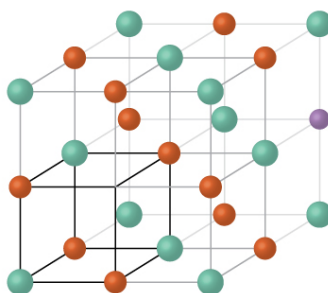
Depending on the relative sizes of the cations and anions, the cations of an ionic compound may occupy tetrahedral or octahedral holes, as illustrated in [\[link\]](#). Relatively small cations occupy tetrahedral holes, and larger cations occupy octahedral holes. If the cations are too large to fit into the

octahedral holes, the anions may adopt a more open structure, such as a simple cubic array. The larger cations can then occupy the larger cubic holes made possible by the more open spacing.



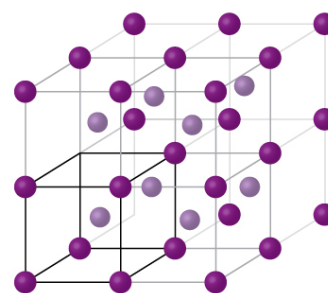
Tetrahedral hole

Cation radius is about 22.5 to 41.4% of the anion radius



Octahedral hole

Cation radius is about 41.4 to 73.2% of the anion radius



Cubic hole

Cation radius is about 73.2 to 100% of the anion radius

A cation's size and the shape of the hole occupied by the compound are directly related.

There are two tetrahedral holes for each anion in either an HCP or CCP array of anions. A compound that crystallizes in a closest-packed array of anions with cations in the tetrahedral holes can have a maximum cation:anion ratio of 2:1; all of the tetrahedral holes are filled at this ratio. Examples include Li_2O , Na_2O , Li_2S , and Na_2S . Compounds with a ratio of less than 2:1 may also crystallize in a closest-packed array of anions with cations in the tetrahedral holes, if the ionic sizes fit. In these compounds, however, some of the tetrahedral holes remain vacant.

Example:

Occupancy of Tetrahedral Holes

Zinc sulfide is an important industrial source of zinc and is also used as a white pigment in paint. Zinc sulfide crystallizes with zinc ions occupying one-half of the tetrahedral holes in a closest-packed array of sulfide ions. What is the formula of zinc sulfide?

Solution

Because there are two tetrahedral holes per anion (sulfide ion) and one-half of these holes are occupied by zinc ions, there must be $\frac{1}{2} \times 2$, or 1, zinc ion per sulfide ion. Thus, the formula is ZnS .

Check Your Learning

Lithium selenide can be described as a closest-packed array of selenide ions with lithium ions in all of the tetrahedral holes. What is the formula of lithium selenide?

Note:

Answer:

Li_2Se

The ratio of octahedral holes to anions in either an HCP or CCP structure is 1:1. Thus, compounds with cations in octahedral holes in a closest-packed array of anions can have a maximum cation:anion ratio of 1:1. In NiO, MnS, NaCl, and KH, for example, all of the octahedral holes are filled. Ratios of less than 1:1 are observed when some of the octahedral holes remain empty.

Example:**Stoichiometry of Ionic Compounds**

Sapphire is aluminum oxide. Aluminum oxide crystallizes with aluminum ions in two-thirds of the octahedral holes in a closest-packed array of oxide ions. What is the formula of aluminum oxide?

Solution

Because there is one octahedral hole per anion (oxide ion) and only two-thirds of these holes are occupied, the ratio of aluminum to oxygen must be $\frac{2}{3}:1$, which would give $\text{Al}_{2/3}\text{O}$. The simplest whole number ratio is 2:3, so the formula is Al_2O_3 .

Check Your Learning

The white pigment titanium oxide crystallizes with titanium ions in one-half of the octahedral holes in a closest-packed array of oxide ions. What is the formula of titanium oxide?

Note:**Answer:**

TiO_2

In a simple cubic array of anions, there is one cubic hole that can be occupied by a cation for each anion in the array. In CsCl, and in other compounds with the same structure, all of the cubic holes are occupied. Half of the cubic holes are occupied in SrH_2 , UO_2 , SrCl_2 , and CaF_2 .

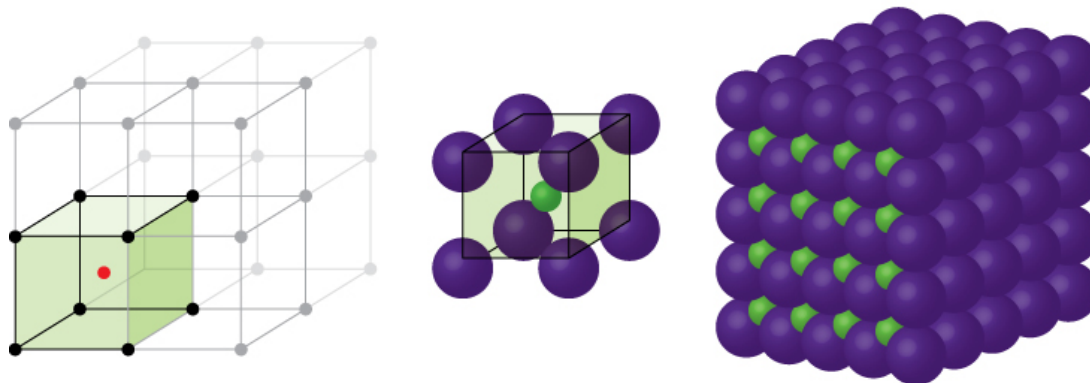
Different types of ionic compounds often crystallize in the same structure when the relative sizes of their ions and their stoichiometries (the two principal features that determine structure) are similar.

Unit Cells of Ionic Compounds

Many ionic compounds crystallize with cubic unit cells, and we will use these compounds to describe the general features of ionic structures.

When an ionic compound is composed of cations and anions of similar size in a 1:1 ratio, it typically forms a simple cubic structure. Cesium chloride, CsCl, (illustrated in [\[link\]](#)) is an example of this, with Cs^+ and Cl^- having radii of 174 pm and 181 pm, respectively. We can think of this as chloride ions forming a simple cubic unit cell, with a cesium ion in the center; or as cesium ions forming a unit cell with a chloride ion in the center; or as simple cubic unit cells formed by Cs^+ ions overlapping unit cells formed by Cl^- ions. Cesium ions and chloride ions touch along the body diagonals of the unit

cells. One cesium ion and one chloride ion are present per unit cell, giving the 1:1 stoichiometry required by the formula for cesium chloride. Note that there is no lattice point in the center of the cell, and CsCl is not a BCC structure because a cesium ion is not identical to a chloride ion.

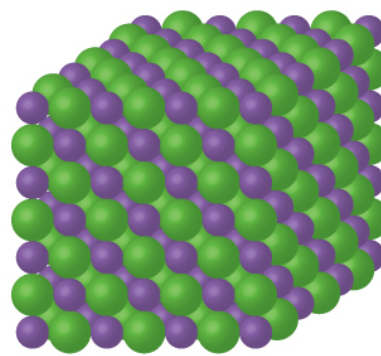
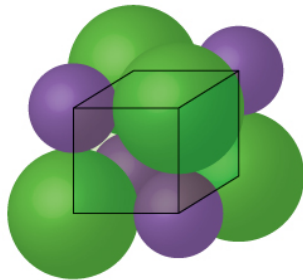
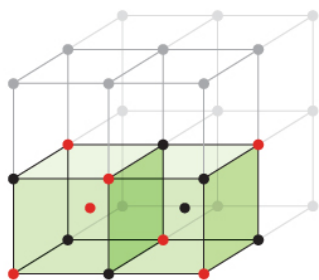


Simple cubic structure

Ionic compounds with similar-sized cations and anions, such as CsCl, usually form a simple cubic structure. They can be described by unit cells with either cations at the corners or anions at the corners.

We have said that the location of lattice points is arbitrary. This is illustrated by an alternate description of the CsCl structure in which the lattice points are located in the centers of the cesium ions. In this description, the cesium ions are located on the lattice points at the corners of the cell, and the chloride ion is located at the center of the cell. The two unit cells are different, but they describe identical structures.

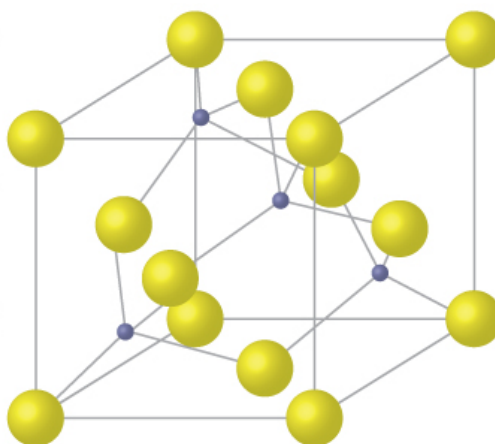
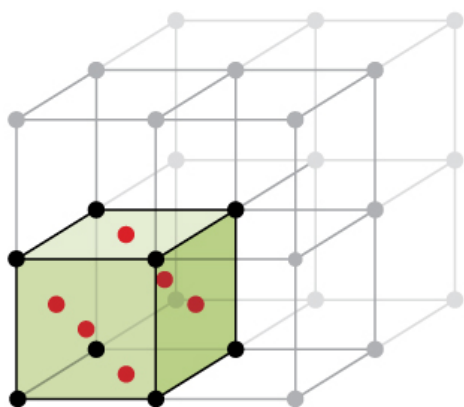
When an ionic compound is composed of a 1:1 ratio of cations and anions that differ significantly in size, it typically crystallizes with an FCC unit cell, like that shown in [\[link\]](#). Sodium chloride, NaCl, is an example of this, with Na^+ and Cl^- having radii of 102 pm and 181 pm, respectively. We can think of this as chloride ions forming an FCC cell, with sodium ions located in the octahedral holes in the middle of the cell edges and in the center of the cell. The sodium and chloride ions touch each other along the cell edges. The unit cell contains four sodium ions and four chloride ions, giving the 1:1 stoichiometry required by the formula, NaCl.



Face-centered simple cubic structure

Ionic compounds with anions that are much larger than cations, such as NaCl, usually form an FCC structure. They can be described by FCC unit cells with cations in the octahedral holes.

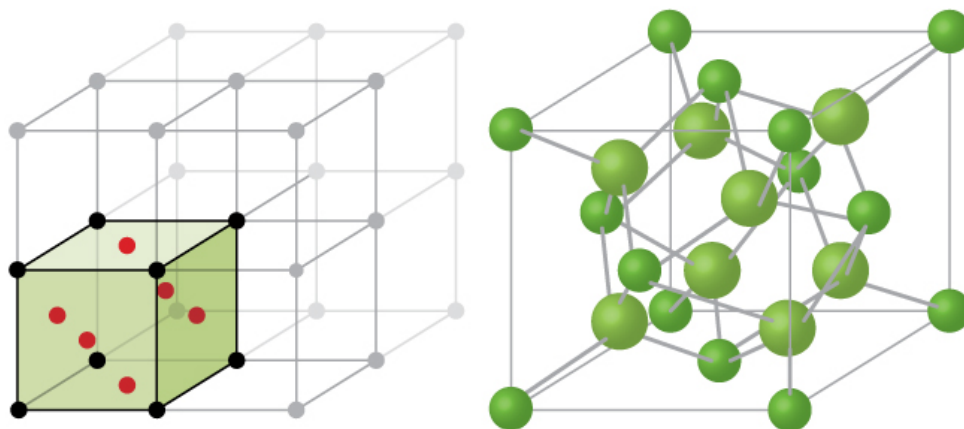
The cubic form of zinc sulfide, zinc blende, also crystallizes in an FCC unit cell, as illustrated in [\[link\]](#). This structure contains sulfide ions on the lattice points of an FCC lattice. (The arrangement of sulfide ions is identical to the arrangement of chloride ions in sodium chloride.) The radius of a zinc ion is only about 40% of the radius of a sulfide ion, so these small Zn^{2+} ions are located in alternating tetrahedral holes, that is, in one half of the tetrahedral holes. There are four zinc ions and four sulfide ions in the unit cell, giving the empirical formula ZnS.



ZnS face-centered unit cell

ZnS, zinc sulfide (or zinc blende) forms an FCC unit cell with sulfide ions at the lattice points and much smaller zinc ions occupying half of the tetrahedral holes in the structure.

A calcium fluoride unit cell, like that shown in [\[link\]](#), is also an FCC unit cell, but in this case, the cations are located on the lattice points; equivalent calcium ions are located on the lattice points of an FCC lattice. All of the tetrahedral sites in the FCC array of calcium ions are occupied by fluoride ions. There are four calcium ions and eight fluoride ions in a unit cell, giving a calcium:fluorine ratio of 1:2, as required by the chemical formula, CaF_2 . Close examination of [\[link\]](#) will reveal a simple cubic array of fluoride ions with calcium ions in one half of the cubic holes. The structure cannot be described in terms of a **space lattice** of points on the fluoride ions because the fluoride ions do not all have identical environments. The orientation of the four calcium ions about the fluoride ions differs.



CaF_2 face-centered unit cell

Calcium fluoride, CaF_2 , forms an FCC unit cell with calcium ions (green) at the lattice points and fluoride ions (red) occupying all of the tetrahedral sites between them.

Calculation of Ionic Radii

If we know the edge length of a unit cell of an ionic compound and the position of the ions in the cell, we can calculate ionic radii for the ions in the compound if we make assumptions about individual ionic shapes and contacts.

Example:

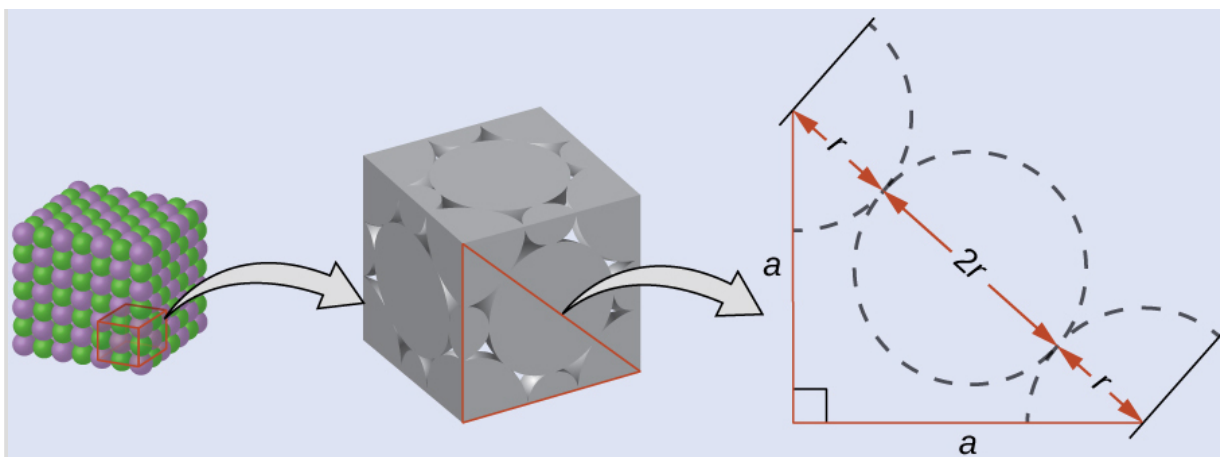
Calculation of Ionic Radii

The edge length of the unit cell of LiCl (NaCl-like structure, FCC) is 0.514 nm or 5.14 Å. Assuming that the lithium ion is small enough so that the chloride ions are in contact, as in [\[link\]](#), calculate the ionic radius for the chloride ion.

Note: The length unit angstrom, Å, is often used to represent atomic-scale dimensions and is equivalent to 10^{-10} m.

Solution

On the face of a LiCl unit cell, chloride ions contact each other across the diagonal of the face:



Drawing a right triangle on the face of the unit cell, we see that the length of the diagonal is equal to four chloride radii (one radius from each corner chloride and one diameter—which equals two radii—from the chloride ion in the center of the face), so $d = 4r$. From the Pythagorean theorem, we have:

Equation:

$$a^2 + a^2 = d^2$$

which yields:

Equation:

$$(0.514 \text{ nm})^2 + (0.514 \text{ nm})^2 = (4r)^2 = 16r^2$$

Solving this gives:

Equation:

$$r = \sqrt{\frac{(0.514 \text{ nm})^2 + (0.514 \text{ nm})^2}{16}} = 0.182 \text{ nm (1.82 \AA)} \text{ for a Cl}^- \text{ radius.}$$

Check Your Learning

The edge length of the unit cell of KCl (NaCl-like structure, FCC) is 6.28 Å. Assuming anion-cation contact along the cell edge, calculate the radius of the potassium ion. The radius of the chloride ion is 1.82 Å.

Note:

Answer:

The radius of the potassium ion is 1.33 Å.

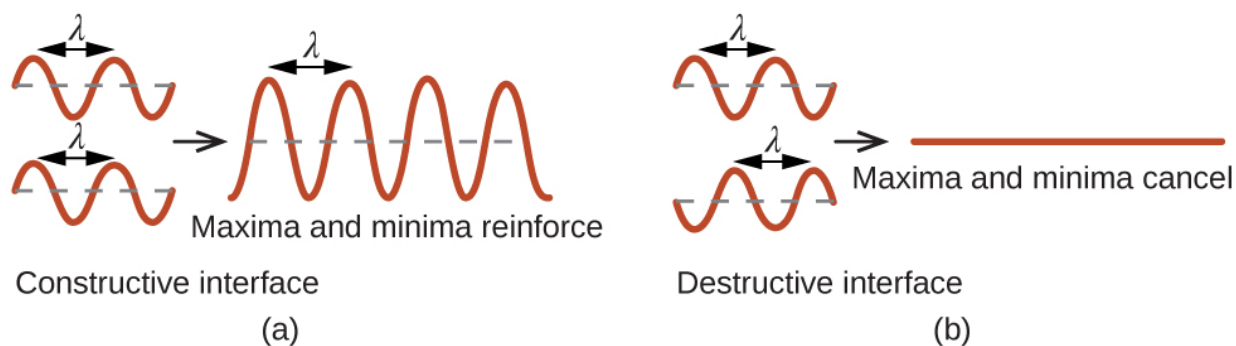
It is important to realize that values for ionic radii calculated from the edge lengths of unit cells depend on numerous assumptions, such as a perfect spherical shape for ions, which are

approximations at best. Hence, such calculated values are themselves approximate and comparisons cannot be pushed too far. Nevertheless, this method has proved useful for calculating ionic radii from experimental measurements such as X-ray crystallographic determinations.

X-Ray Crystallography

The size of the unit cell and the arrangement of atoms in a crystal may be determined from measurements of the *diffraction* of X-rays by the crystal, termed **X-ray crystallography**. **Diffraction** is the change in the direction of travel experienced by an electromagnetic wave when it encounters a physical barrier whose dimensions are comparable to those of the wavelength of the light. X-rays are electromagnetic radiation with wavelengths about as long as the distance between neighboring atoms in crystals (on the order of a few Å).

When a beam of monochromatic X-rays strikes a crystal, its rays are scattered in all directions by the atoms within the crystal. When scattered waves traveling in the same direction encounter one another, they undergo *interference*, a process by which the waves combine to yield either an increase or a decrease in amplitude (intensity) depending upon the extent to which the combining waves' maxima are separated (see [\[link\]](#)).



Light waves occupying the same space experience interference, combining to yield waves of greater (a) or lesser (b) intensity, depending upon the separation of their maxima and minima.

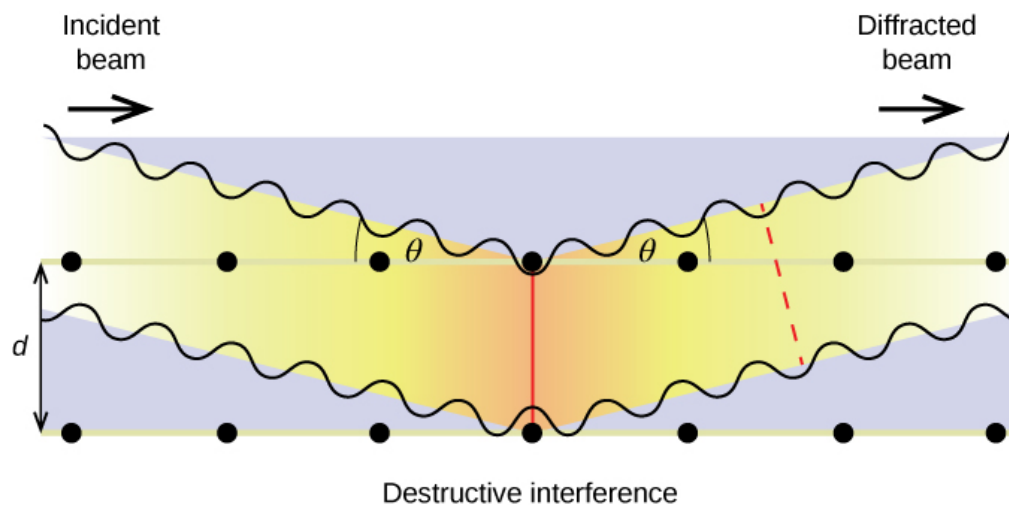
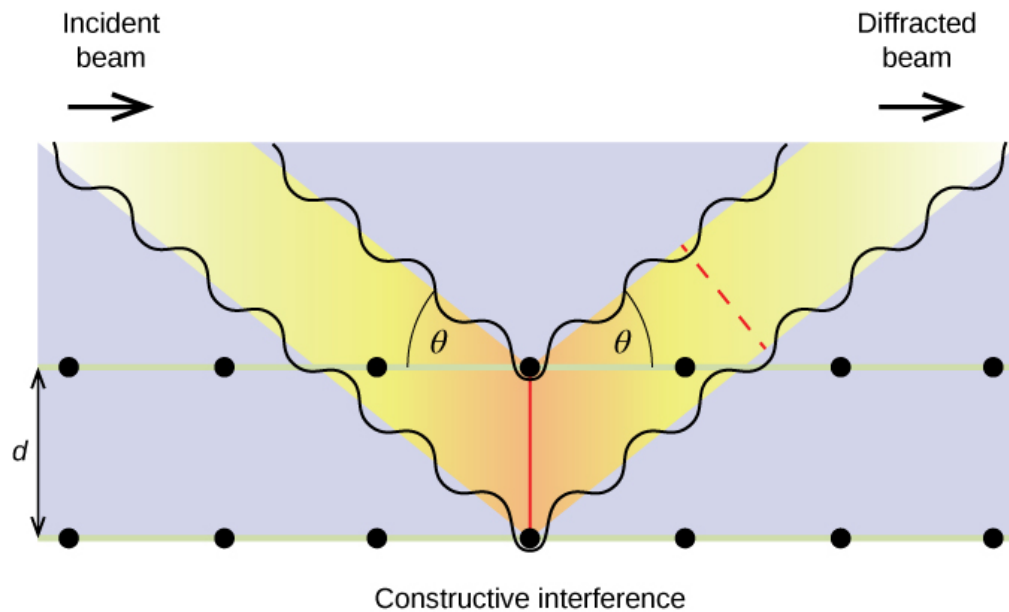
When X-rays of a certain wavelength, λ , are scattered by atoms in adjacent crystal planes separated by a distance, d , they may undergo constructive interference when the difference between the distances traveled by the two waves prior to their combination is an integer factor, n , of the wavelength. This condition is satisfied when the angle of the diffracted beam, θ , is related to the wavelength and interatomic distance by the equation:

Equation:

$$n\lambda = 2d \sin \theta$$

This relation is known as the **Bragg equation** in honor of W. H. Bragg, the English physicist who first explained this phenomenon. [\[link\]](#) illustrates two examples of diffracted waves from the same two crystal planes. The figure on the left depicts waves diffracted at the Bragg angle, resulting in

constructive interference, while that on the right shows diffraction and a different angle that does not satisfy the Bragg condition, resulting in destructive interference.



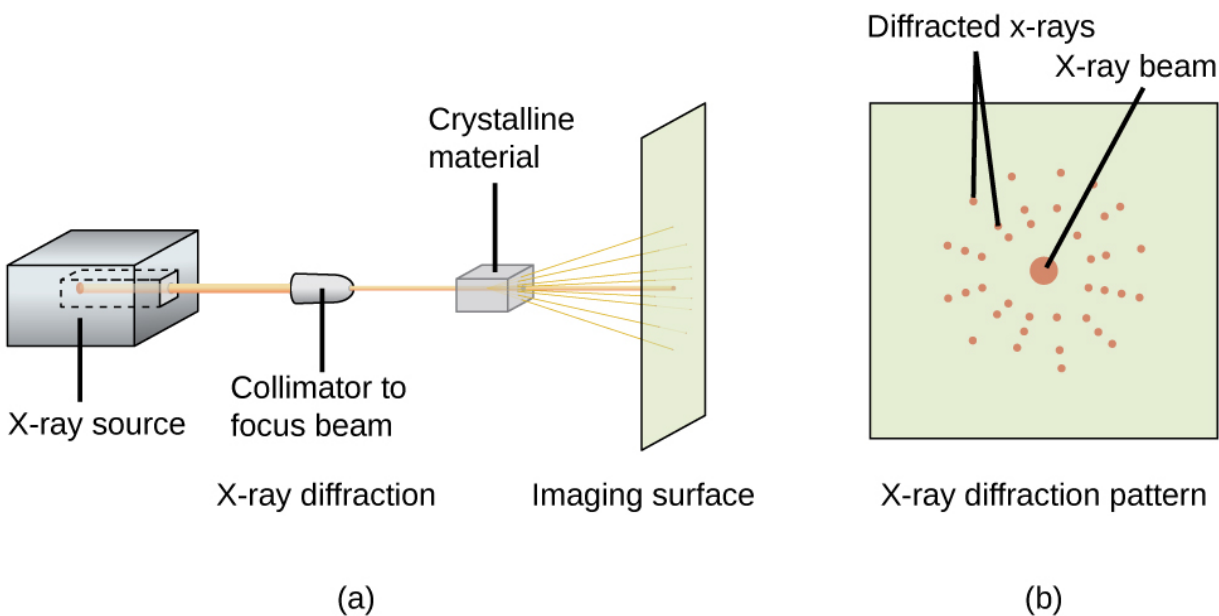
The diffraction of X-rays scattered by the atoms within a crystal permits the determination of the distance between the atoms. The top image depicts constructive interference between two scattered waves and a resultant diffracted wave of high intensity. The bottom image depicts destructive interference and a low intensity diffracted wave.

Note:



Visit this [site](#) for more details on the Bragg equation and a simulator that allows you to explore the effect of each variable on the intensity of the diffracted wave.

An X-ray diffractometer, such as the one illustrated in [\[link\]](#), may be used to measure the angles at which X-rays are diffracted when interacting with a crystal as described earlier. From such measurements, the Bragg equation may be used to compute distances between atoms as demonstrated in the following example exercise.



(a) In a diffractometer, a beam of X-rays strikes a crystalline material, producing (b) an X-ray diffraction pattern that can be analyzed to determine the crystal structure.

Example:
Using the Bragg Equation

In a diffractometer, X-rays with a wavelength of 0.1315 nm were used to produce a diffraction pattern for copper. The first order diffraction ($n = 1$) occurred at an angle $\theta = 25.25^\circ$. Determine the spacing between the diffracting planes in copper.

Solution

The distance between the planes is found by solving the Bragg equation, $n\lambda = 2d \sin \theta$, for d .

This gives: $d = \frac{n\lambda}{2 \sin \theta} = \frac{1(0.1315 \text{ nm})}{2 \sin (25.25^\circ)} = 0.154 \text{ nm}$

Check Your Learning

A crystal with spacing between planes equal to 0.394 nm diffracts X-rays with a wavelength of 0.147 nm. What is the angle for the first order diffraction?

Note:**Answer:**

21.9°.

Note:**X-ray Crystallographer Rosalind Franklin**

The discovery of the structure of DNA in 1953 by Francis Crick and James Watson is one of the great achievements in the history of science. They were awarded the 1962 Nobel Prize in Physiology or Medicine, along with Maurice Wilkins, who provided experimental proof of DNA's structure. British chemist Rosalind Franklin made invaluable contributions to this monumental achievement through her work in measuring X-ray diffraction images of DNA. Early in her career, Franklin's research on the structure of coals proved helpful to the British war effort. After shifting her focus to biological systems in the early 1950s, Franklin and doctoral student Raymond Gosling discovered that DNA consists of two forms: a long, thin fiber formed when wet (type "B") and a short, wide fiber formed when dried (type "A"). Her X-ray diffraction images of DNA ([link](#)) provided the crucial information that allowed Watson and Crick to confirm that DNA forms a double helix, and to determine details of its size and structure. Franklin also conducted pioneering research on viruses and the RNA that contains their genetic information, uncovering new information that radically changed the body of knowledge in the field. After developing ovarian cancer, Franklin continued to work until her death in 1958 at age 37. Among many posthumous recognitions of her work, the Chicago Medical School of Finch University of Health Sciences changed its name to the Rosalind Franklin University of Medicine and Science in 2004, and adopted an image of her famous X-ray diffraction image of DNA as its official university logo.



This illustration shows an X-ray diffraction image similar to the one Franklin found in her research.
(credit: National Institutes of Health)

Key Concepts and Summary

The structures of crystalline metals and simple ionic compounds can be described in terms of packing of spheres. Metal atoms can pack in hexagonal closest-packed structures, cubic closest-packed structures, body-centered structures, and simple cubic structures. The anions in simple ionic structures commonly adopt one of these structures, and the cations occupy the spaces remaining between the anions. Small cations usually occupy tetrahedral holes in a closest-packed array of anions. Larger cations usually occupy octahedral holes. Still larger cations can occupy cubic holes in a simple cubic array of anions. The structure of a solid can be described by indicating the size and shape of a unit cell and the contents of the cell. The type of structure and dimensions of the unit cell can be determined by X-ray diffraction measurements.

Key Equations

- $n\lambda = 2d \sin \theta$

Chemistry End of Chapter Exercises

Exercise:

Problem:

Describe the crystal structure of iron, which crystallizes with two equivalent metal atoms in a cubic unit cell.

Solution:

The structure of this low-temperature form of iron (below 910 °C) is body-centered cubic. There is one-eighth atom at each of the eight corners of the cube and one atom in the center of the cube.

Exercise:**Problem:**

Describe the crystal structure of Pt, which crystallizes with four equivalent metal atoms in a cubic unit cell.

Exercise:**Problem:**

What is the coordination number of a chromium atom in the body-centered cubic structure of chromium?

Solution:

eight

Exercise:**Problem:**

What is the coordination number of an aluminum atom in the face-centered cubic structure of aluminum?

Exercise:**Problem:**

Cobalt metal crystallizes in a hexagonal closest packed structure. What is the coordination number of a cobalt atom?

Solution:

12

Exercise:**Problem:**

Nickel metal crystallizes in a cubic closest packed structure. What is the coordination number of a nickel atom?

Exercise:

Problem:

Tungsten crystallizes in a body-centered cubic unit cell with an edge length of 3.165 Å.

- (a) What is the atomic radius of tungsten in this structure?
 - (b) Calculate the density of tungsten.
-

Solution:

- (a) 1.370 Å; (b) 19.26 g/cm

Exercise:**Problem:**

Platinum (atomic radius = 1.38 Å) crystallizes in a cubic closely packed structure. Calculate the edge length of the face-centered cubic unit cell and the density of platinum.

Exercise:

Problem: Barium crystallizes in a body-centered cubic unit cell with an edge length of 5.025 Å

- (a) What is the atomic radius of barium in this structure?
 - (b) Calculate the density of barium.
-

Solution:

- (a) 2.176 Å; (b) 3.595 g/cm³

Exercise:**Problem:**

Aluminum (atomic radius = 1.43 Å) crystallizes in a cubic closely packed structure. Calculate the edge length of the face-centered cubic unit cell and the density of aluminum.

Exercise:**Problem:**

The density of aluminum is 2.7 g/cm³; that of silicon is 2.3 g/cm³. Explain why Si has the lower density even though it has heavier atoms.

Solution:

The crystal structure of Si shows that it is less tightly packed (coordination number 4) in the solid than Al (coordination number 12).

Exercise:

Problem:

The free space in a metal may be found by subtracting the volume of the atoms in a unit cell from the volume of the cell. Calculate the percentage of free space in each of the three cubic lattices if all atoms in each are of equal size and touch their nearest neighbors. Which of these structures represents the most efficient packing? That is, which packs with the least amount of unused space?

Exercise:**Problem:**

Cadmium sulfide, sometimes used as a yellow pigment by artists, crystallizes with cadmium, occupying one-half of the tetrahedral holes in a closest packed array of sulfide ions. What is the formula of cadmium sulfide? Explain your answer.

Solution:

In a closest-packed array, two tetrahedral holes exist for each anion. If only half the tetrahedral holes are occupied, the numbers of anions and cations are equal. The formula for cadmium sulfide is CdS.

Exercise:**Problem:**

A compound of cadmium, tin, and phosphorus is used in the fabrication of some semiconductors. It crystallizes with cadmium occupying one-fourth of the tetrahedral holes and tin occupying one-fourth of the tetrahedral holes in a closest packed array of phosphide ions. What is the formula of the compound? Explain your answer.

Exercise:**Problem:**

What is the formula of the magnetic oxide of cobalt, used in recording tapes, that crystallizes with cobalt atoms occupying one-eighth of the tetrahedral holes and one-half of the octahedral holes in a closely packed array of oxide ions?

Solution:**Exercise:****Problem:**

A compound containing zinc, aluminum, and sulfur crystallizes with a closest-packed array of sulfide ions. Zinc ions are found in one-eighth of the tetrahedral holes and aluminum ions in one-half of the octahedral holes. What is the empirical formula of the compound?

Exercise:

Problem:

A compound of thallium and iodine crystallizes in a simple cubic array of iodide ions with thallium ions in all of the cubic holes. What is the formula of this iodide? Explain your answer.

Solution:

In a simple cubic array, only one cubic hole can be occupied by a cation for each anion in the array. The ratio of thallium to iodide must be 1:1; therefore, the formula for thallium is TlI.

Exercise:**Problem:**

Which of the following elements reacts with sulfur to form a solid in which the sulfur atoms form a closest-packed array with all of the octahedral holes occupied: Li, Na, Be, Ca, or Al?

Exercise:**Problem:**

What is the percent by mass of titanium in rutile, a mineral that contains titanium and oxygen, if structure can be described as a closest packed array of oxide ions with titanium ions in one-half of the octahedral holes? What is the oxidation number of titanium?

Solution:

59.95%; The oxidation number of titanium is +4.

Exercise:**Problem:**

Explain why the chemically similar alkali metal chlorides NaCl and CsCl have different structures, whereas the chemically different NaCl and MnS have the same structure.

Exercise:**Problem:**

As minerals were formed from the molten magma, different ions occupied the same sites in the crystals. Lithium often occurs along with magnesium in minerals despite the difference in the charge on their ions. Suggest an explanation.

Solution:

Both ions are close in size: Mg, 0.65; Li, 0.60. This similarity allows the two to interchange rather easily. The difference in charge is generally compensated by the switch of Si^{4+} for Al^{3+} .

Exercise:**Problem:**

Rubidium iodide crystallizes with a cubic unit cell that contains iodide ions at the corners and a rubidium ion in the center. What is the formula of the compound?

Exercise:

Problem:

One of the various manganese oxides crystallizes with a cubic unit cell that contains manganese ions at the corners and in the center. Oxide ions are located at the center of each edge of the unit cell. What is the formula of the compound?

Solution:**Exercise:****Problem:**

NaH crystallizes with the same crystal structure as NaCl. The edge length of the cubic unit cell of NaH is 4.880 Å.

- (a) Calculate the ionic radius of H^- . (The ionic radius of Li^+ is 0.095 Å.)
- (b) Calculate the density of NaH.

Exercise:**Problem:**

Thallium(I) iodide crystallizes with the same structure as CsCl. The edge length of the unit cell of TlI is 4.20 Å. Calculate the ionic radius of Tl^+ . (The ionic radius of I^- is 2.16 Å.)

Solution:

$$1.48 \text{ Å}$$

Exercise:**Problem:**

A cubic unit cell contains manganese ions at the corners and fluoride ions at the center of each edge.

- (a) What is the empirical formula of this compound? Explain your answer.
- (b) What is the coordination number of the Mn^{3+} ion?
- (c) Calculate the edge length of the unit cell if the radius of a Mn^{3+} ion is 0.65 Å.
- (d) Calculate the density of the compound.

Exercise:**Problem:**

What is the spacing between crystal planes that diffract X-rays with a wavelength of 1.541 nm at an angle θ of 15.55° (first order reflection)?

Solution:

2.874 Å

Exercise:

Problem:

A diffractometer using X-rays with a wavelength of 0.2287 nm produced first-order diffraction peak for a crystal angle $\theta = 16.21^\circ$. Determine the spacing between the diffracting planes in this crystal.

Exercise:

Problem:

A metal with spacing between planes equal to 0.4164 nm diffracts X-rays with a wavelength of 0.2879 nm. What is the diffraction angle for the first order diffraction peak?

Solution:

20.2°

Exercise:

Problem:

Gold crystallizes in a face-centered cubic unit cell. The second-order reflection ($n = 2$) of X-rays for the planes that make up the tops and bottoms of the unit cells is at $\theta = 22.20^\circ$. The wavelength of the X-rays is 1.54 Å. What is the density of metallic gold?

Exercise:

Problem:

When an electron in an excited molybdenum atom falls from the L to the K shell, an X-ray is emitted. These X-rays are diffracted at an angle of 7.75° by planes with a separation of 2.64 Å. What is the difference in energy between the K shell and the L shell in molybdenum assuming a first-order diffraction?

Solution:

1.74×10^4 eV

Glossary

body-centered cubic (BCC) solid

crystalline structure that has a cubic unit cell with lattice points at the corners and in the center of the cell

body-centered cubic unit cell

simplest repeating unit of a body-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of the cube

Bragg equation

equation that relates the angles at which X-rays are diffracted by the atoms within a crystal

coordination number

number of atoms closest to any given atom in a crystal or to the central metal atom in a complex

cubic closest packing (CCP)

crystalline structure in which planes of closely packed atoms or ions are stacked as a series of three alternating layers of different relative orientations (ABC)

diffraction

redirection of electromagnetic radiation that occurs when it encounters a physical barrier of appropriate dimensions

face-centered cubic (FCC) solid

crystalline structure consisting of a cubic unit cell with lattice points on the corners and in the center of each face

face-centered cubic unit cell

simplest repeating unit of a face-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of each face

hexagonal closest packing (HCP)

crystalline structure in which close packed layers of atoms or ions are stacked as a series of two alternating layers of different relative orientations (AB)

hole

(also, interstice) space between atoms within a crystal

isomorphous

possessing the same crystalline structure

octahedral hole

open space in a crystal at the center of six particles located at the corners of an octahedron

simple cubic unit cell

(also, primitive cubic unit cell) unit cell in the simple cubic structure

simple cubic structure

crystalline structure with a cubic unit cell with lattice points only at the corners

space lattice

all points within a crystal that have identical environments

tetrahedral hole

tetrahedral space formed by four atoms or ions in a crystal

unit cell

smallest portion of a space lattice that is repeated in three dimensions to form the entire lattice

X-ray crystallography

experimental technique for determining distances between atoms in a crystal by measuring the angles at which X-rays are diffracted when passing through the crystal

Introduction

class="introduction"

- The Dissolution Process
- Electrolytes
- Solubility
- Colligative Properties
- Colloids

Coral reefs, such as this one at the Palmyra Atoll National Wildlife Refuge, are vital to the ecosystem of earth's oceans but are threatened by climate change and dissolved pollution. Marine life depends on the specific chemical composition of the complex mixture we know as seawater. (credit: modification of work by "USFWS – Pacific Region"/Wikimedia Commons)



Coral reefs are home to about 25% of all marine species. They are being threatened by climate change, oceanic acidification, and water pollution, all of which change the composition of the solution we know as seawater. Dissolved oxygen in seawater is critical for sea creatures, but as the oceans warm, oxygen becomes less soluble. As the concentration of carbon dioxide in the atmosphere increases, the concentration of carbon dioxide in the oceans increases, contributing to oceanic acidification. Coral reefs are particularly sensitive to the acidification of the ocean, since the exoskeletons of the coral polyps are soluble in acidic solutions. Humans contribute to the changing of seawater composition by allowing agricultural runoff and other forms of pollution to affect our oceans.

Solutions are crucial to the processes that sustain life and to many other processes involving chemical reactions. In this chapter, we will consider the nature of solutions, and examine factors that determine whether a solution will form and what properties it may have. In addition, we will discuss colloids—systems that resemble solutions but consist of dispersions of particles somewhat larger than ordinary molecules or ions.

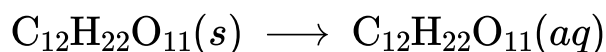
The Dissolution Process

By the end of this section, you will be able to:

- Describe the basic properties of solutions and how they form
- Predict whether a given mixture will yield a solution based on molecular properties of its components
- Explain why some solutions either produce or absorb heat when they form

An earlier chapter of this text introduced *solutions*, defined as homogeneous mixtures of two or more substances. Often, one component of a solution is present at a significantly greater concentration, in which case it is called the *solvent*. The other components of the solution present in relatively lesser concentrations are called *solutes*. Sugar is a covalent solid composed of sucrose molecules, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. When this compound dissolves in water, its molecules become uniformly distributed among the molecules of water:

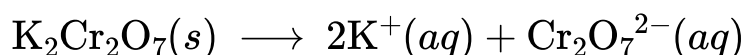
Equation:



The subscript “*aq*” in the equation signifies that the sucrose molecules are solutes and are therefore *individually dispersed* throughout the *aqueous solution* (water is the solvent). Although sucrose molecules are heavier than water molecules, they remain dispersed throughout the solution; gravity does not cause them to “settle out” over time.

Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, is an ionic compound composed of colorless potassium ions, K^+ , and orange dichromate ions, $\text{Cr}_2\text{O}_7^{2-}$. When a small amount of solid potassium dichromate is added to water, the compound dissolves and dissociates to yield potassium ions and dichromate ions uniformly distributed throughout the mixture ([\[link\]](#)), as indicated in this equation:

Equation:



As with the mixture of sugar and water, this mixture is also an aqueous solution. Its solutes, potassium and dichromate ions, remain individually dispersed among the solvent (water) molecules.



When potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) is mixed with water, it forms a homogeneous orange solution. (credit: modification of work by Mark Ott)

Note:



Visit this [virtual lab](#) to view simulations of the dissolution of common covalent and ionic substances (sugar and salt) in water.

Water is used so often as a solvent that the word solution has come to imply an aqueous solution to many people. However, almost any gas, liquid, or solid can act as a solvent. Many **alloys** are solid solutions of one metal dissolved in another; for example, US five-cent coins contain nickel dissolved in copper. Air is a gaseous solution, a homogeneous mixture of nitrogen, oxygen, and several other gases. Oxygen (a gas), alcohol (a

liquid), and sugar (a solid) all dissolve in water (a liquid) to form liquid solutions. [\[link\]](#) gives examples of several different solutions and the phases of the solutes and solvents.

Different Types of Solutions		
Solution	Solute	Solvent
air	$O_2(g)$	$N_2(g)$
soft drinks [footnote] If bubbles of gas are observed within the liquid, the mixture is not homogeneous and, thus, not a solution.	$CO_2(g)$	$H_2O(l)$
hydrogen in palladium	$H_2(g)$	$Pd(s)$
rubbing alcohol	$H_2O(l)$	$C_3H_8O(l)$ (2-propanol)
saltwater	$NaCl(s)$	$H_2O(l)$
brass	$Zn(s)$	$Cu(s)$

Solutions exhibit these defining traits:

- They are homogeneous; that is, after a solution is mixed, it has the same composition at all points throughout (its composition is uniform).
- The physical state of a solution—solid, liquid, or gas—is typically the same as that of the solvent, as demonstrated by the examples in [\[link\]](#).

- The components of a solution are dispersed on a molecular scale; that is, they consist of a mixture of separated molecules, atoms, and/or ions.
- The dissolved solute in a solution will not settle out or separate from the solvent.
- The composition of a solution, or the concentrations of its components, can be varied continuously, within limits.

The Formation of Solutions

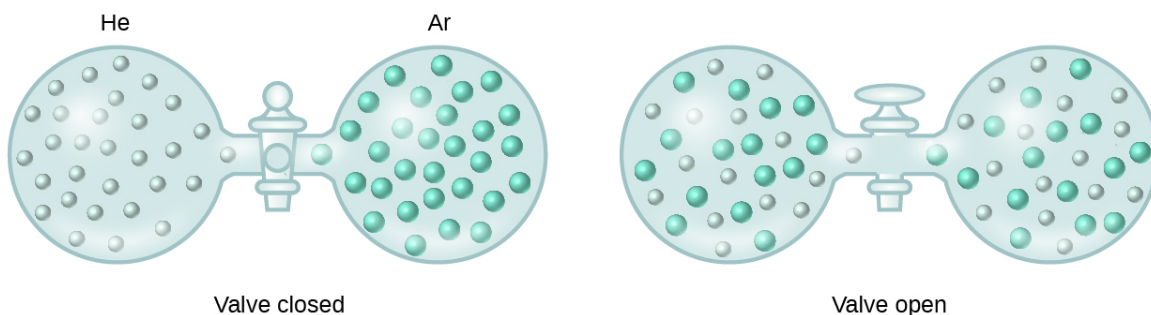
The formation of a solution is an example of a **spontaneous process**, a process that occurs under specified conditions without the requirement of energy from some external source. Sometimes we stir a mixture to speed up the dissolution process, but this is not necessary; a homogeneous solution would form if we waited long enough. The topic of spontaneity is critically important to the study of chemical thermodynamics and is treated more thoroughly in a later chapter of this text. For purposes of this chapter's discussion, it will suffice to consider two criteria that *favor*, but do not guarantee, the spontaneous formation of a solution:

1. a decrease in the internal energy of the system (an exothermic change, as discussed in the previous chapter on thermochemistry)
2. an increase in the disorder in the system (which indicates an increase in the *entropy* of the system, as you will learn about in the later chapter on thermodynamics)

In the process of dissolution, an internal energy change often, but not always, occurs as heat is absorbed or evolved. An increase in disorder always results when a solution forms.

When the strengths of the intermolecular forces of attraction between solute and solvent species in a solution are no different than those present in the separated components, the solution is formed with no accompanying energy change. Such a solution is called an **ideal solution**. A mixture of ideal gases (or gases such as helium and argon, which closely approach ideal behavior) is an example of an ideal solution, since the entities comprising these gases experience no significant intermolecular attractions.

When containers of helium and argon are connected, the gases spontaneously mix due to diffusion and form a solution ([\[link\]](#)). The formation of this solution clearly involves an increase in disorder, since the helium and argon atoms occupy a volume twice as large as that which each occupied before mixing.

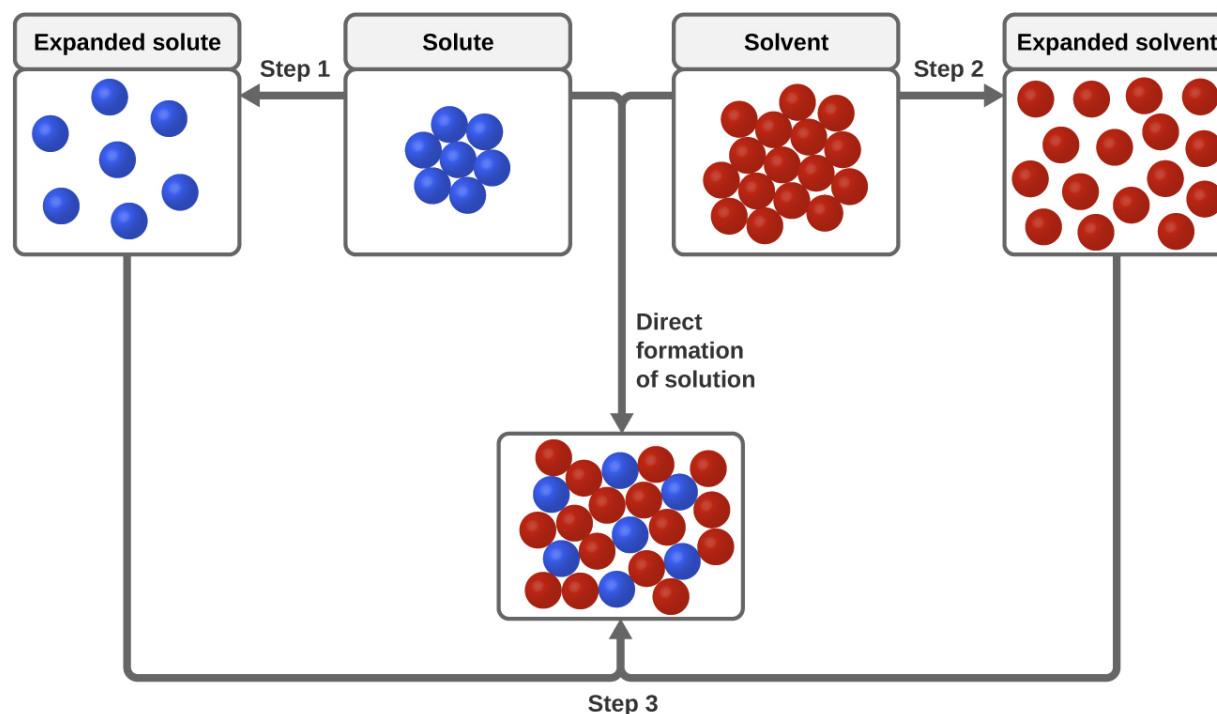


Samples of helium and argon spontaneously mix to give a solution in which the disorder of the atoms of the two gases is increased.

Ideal solutions may also form when structurally similar liquids are mixed. For example, mixtures of the alcohols methanol (CH_3OH) and ethanol ($\text{C}_2\text{H}_5\text{OH}$) form ideal solutions, as do mixtures of the hydrocarbons pentane, C_5H_{12} , and hexane, C_6H_{14} . Placing methanol and ethanol, or pentane and hexane, in the bulbs shown in [\[link\]](#) will result in the same diffusion and subsequent mixing of these liquids as is observed for the He and Ar gases (although at a much slower rate), yielding solutions with no significant change in energy. Unlike a mixture of gases, however, the components of these liquid-liquid solutions do, indeed, experience intermolecular attractive forces. But since the molecules of the two substances being mixed are structurally very similar, the intermolecular attractive forces between like and unlike molecules are essentially the same, and the dissolution process, therefore, does not entail any appreciable increase or decrease in energy. These examples illustrate how diffusion alone can provide the driving force required to cause the spontaneous formation of a solution. In some cases, however, the relative magnitudes of

intermolecular forces of attraction between solute and solvent species may prevent dissolution.

Three types of intermolecular attractive forces are relevant to the dissolution process: solute-solute, solvent-solvent, and solute-solvent. As illustrated in [\[link\]](#), the formation of a solution may be viewed as a stepwise process in which energy is consumed to overcome solute-solute and solvent-solvent attractions (endothermic processes) and released when solute-solvent attractions are established (an exothermic process referred to as **solvation**). The relative magnitudes of the energy changes associated with these stepwise processes determine whether the dissolution process overall will release or absorb energy. In some cases, solutions do not form because the energy required to separate solute and solvent species is so much greater than the energy released by solvation.



This schematic representation of dissolution shows a stepwise process involving the endothermic separation of solute and solvent species

(Steps 1 and 2) and exothermic solvation (Step 3).

For example, cooking oils and water will not mix to any appreciable extent to yield solutions ([\[link\]](#)). Hydrogen bonding is the dominant intermolecular attractive force present in liquid water; the nonpolar hydrocarbon molecules of cooking oils are not capable of hydrogen bonding, instead being held together by dispersion forces. Forming an oil-water solution would require overcoming the very strong hydrogen bonding in water, as well as the significantly strong dispersion forces between the relatively large oil molecules. And, since the polar water molecules and nonpolar oil molecules would not experience very strong intermolecular attraction, very little energy would be released by solvation.



A mixture of nonpolar cooking oil and polar water does not yield a solution. (credit: Gautam Dogra)

On the other hand, a mixture of ethanol and water will mix in any proportions to yield a solution. In this case, both substances are capable of hydrogen bonding, and so the solvation process is sufficiently exothermic to compensate for the endothermic separations of solute and solvent molecules.

As noted at the beginning of this module, spontaneous solution formation is favored, but not guaranteed, by exothermic dissolution processes. While

many soluble compounds do, indeed, dissolve with the release of heat, some dissolve endothermically. Ammonium nitrate (NH_4NO_3) is one such example and is used to make instant cold packs for treating injuries like the one pictured in [\[link\]](#). A thin-walled plastic bag of water is sealed inside a larger bag with solid NH_4NO_3 . When the smaller bag is broken, a solution of NH_4NO_3 forms, absorbing heat from the surroundings (the injured area to which the pack is applied) and providing a cold compress that decreases swelling. Endothermic dissolutions such as this one require a greater energy input to separate the solute species than is recovered when the solutes are solvated, but they are spontaneous nonetheless due to the increase in disorder that accompanies formation of the solution.



An instant cold pack gets cold when certain salts, such as ammonium

nitrate, dissolve in water—an endothermic process.

Note:



Watch this brief [video](#) illustrating endothermic and exothermic dissolution processes.

Key Concepts and Summary

A solution forms when two or more substances combine physically to yield a mixture that is homogeneous at the molecular level. The solvent is the most concentrated component and determines the physical state of the solution. The solutes are the other components typically present at concentrations less than that of the solvent. Solutions may form endothermically or exothermically, depending upon the relative magnitudes of solute and solvent intermolecular attractive forces. Ideal solutions form with no appreciable change in energy.

Chemistry End of Chapter Exercises

Exercise:

Problem:

How do solutions differ from compounds? From other mixtures?

Solution:

A solution can vary in composition, while a compound cannot vary in composition. Solutions are homogeneous at the molecular level, while other mixtures are heterogeneous.

Exercise:**Problem:**

Which of the principal characteristics of solutions can we see in the solutions of $\text{K}_2\text{Cr}_2\text{O}_7$ shown in [\[link\]](#)?

Exercise:**Problem:**

When KNO_3 is dissolved in water, the resulting solution is significantly colder than the water was originally.

- (a) Is the dissolution of KNO_3 an endothermic or an exothermic process?
 - (b) What conclusions can you draw about the intermolecular attractions involved in the process?
 - (c) Is the resulting solution an ideal solution?
-

Solution:

(a) The process is endothermic as the solution is consuming heat. (b) Attraction between the K^+ and NO_3^- ions is stronger than between the ions and water molecules (the ion-ion interactions have a lower, more negative energy). Therefore, the dissolution process increases the energy of the molecular interactions, and it consumes the thermal

energy of the solution to make up for the difference. (c) No, an ideal solution is formed with no appreciable heat release or consumption.

Exercise:

Problem: Give an example of each of the following types of solutions:

(a) a gas in a liquid

(b) a gas in a gas

(c) a solid in a solid

Exercise:

Problem:

Indicate the most important types of intermolecular attractions in each of the following solutions:

(a) The solution in [\[link\]](#).

(b) $\text{NO}(l)$ in $\text{CO}(l)$

(c) $\text{Cl}_2(g)$ in $\text{Br}_2(l)$

(d) $\text{HCl}(g)$ in benzene $\text{C}_6\text{H}_6(l)$

(e) Methanol $\text{CH}_3\text{OH}(l)$ in $\text{H}_2\text{O}(l)$

Solution:

(a) ion-dipole forces; (b) dipole-dipole forces; (c) dispersion forces; (d) dispersion forces; (e) hydrogen bonding

Exercise:

Problem:

Predict whether each of the following substances would be more soluble in water (polar solvent) or in a hydrocarbon such as heptane (C_7H_{16} , nonpolar solvent):

- (a) vegetable oil (nonpolar)
- (b) isopropyl alcohol (polar)
- (c) potassium bromide (ionic)

Exercise:**Problem:**

Heat is released when some solutions form; heat is absorbed when other solutions form. Provide a molecular explanation for the difference between these two types of spontaneous processes.

Solution:

Heat is released when the total intermolecular forces (IMFs) between the solute and solvent molecules are stronger than the total IMFs in the pure solute and in the pure solvent: Breaking weaker IMFs and forming stronger IMFs releases heat. Heat is absorbed when the total IMFs in the solution are weaker than the total of those in the pure solute and in the pure solvent: Breaking stronger IMFs and forming weaker IMFs absorbs heat.

Exercise:**Problem:**

Solutions of hydrogen in palladium may be formed by exposing Pd metal to H_2 gas. The concentration of hydrogen in the palladium depends on the pressure of H_2 gas applied, but in a more complex fashion than can be described by Henry's law. Under certain conditions, 0.94 g of hydrogen gas is dissolved in 215 g of palladium metal (solution density = 10.8 g cm^3).

- (a) Determine the molarity of this solution.
- (b) Determine the molality of this solution.
- (c) Determine the percent by mass of hydrogen atoms in this solution.

Glossary

alloy

solid mixture of a metallic element and one or more additional elements

ideal solution

solution that forms with no accompanying energy change

solvation

exothermic process in which intermolecular attractive forces between the solute and solvent in a solution are established

spontaneous process

physical or chemical change that occurs without the addition of energy from an external source

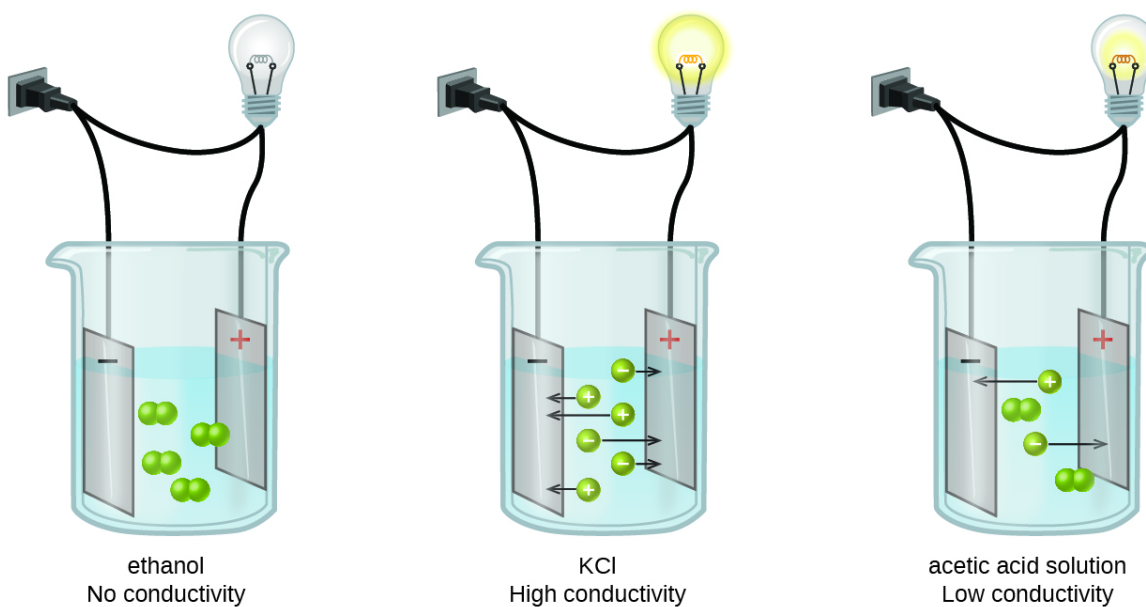
Electrolytes

By the end of this module, you will be able to:

- Define and give examples of electrolytes
- Distinguish between the physical and chemical changes that accompany dissolution of ionic and covalent electrolytes
- Relate electrolyte strength to solute-solvent attractive forces

When some substances are dissolved in water, they undergo either a physical or a chemical change that yields ions in solution. These substances constitute an important class of compounds called **electrolytes**. Substances that do not yield ions when dissolved are called **nonelectrolytes**. If the physical or chemical process that generates the ions is essentially 100% efficient (all of the dissolved compound yields ions), then the substance is known as a **strong electrolyte**. If only a relatively small fraction of the dissolved substance undergoes the ion-producing process, it is called a **weak electrolyte**.

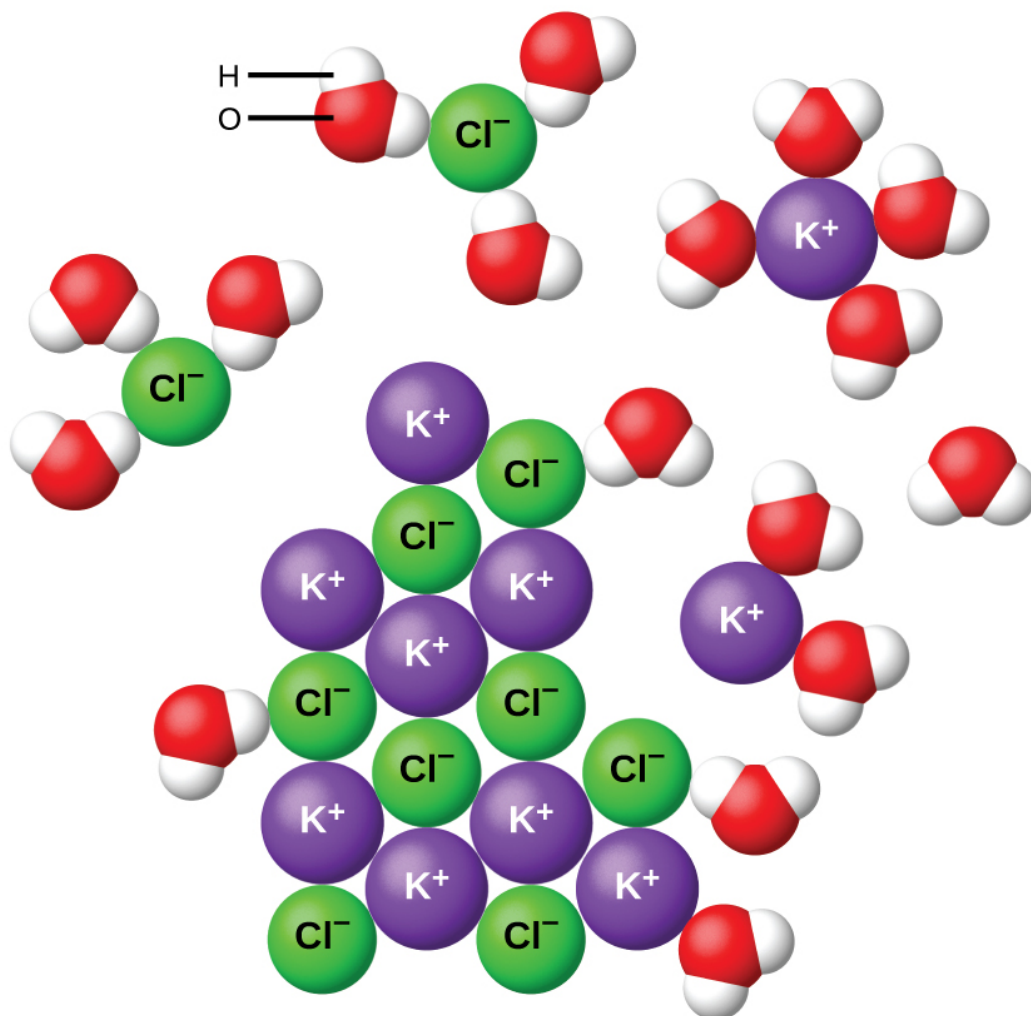
Substances may be identified as strong, weak, or nonelectrolytes by measuring the electrical conductance of an aqueous solution containing the substance. To conduct electricity, a substance must contain freely mobile, charged species. Most familiar is the conduction of electricity through metallic wires, in which case the mobile, charged entities are electrons. Solutions may also conduct electricity if they contain dissolved ions, with conductivity increasing as ion concentration increases. Applying a voltage to electrodes immersed in a solution permits assessment of the relative concentration of dissolved ions, either quantitatively, by measuring the electrical current flow, or qualitatively, by observing the brightness of a light bulb included in the circuit ([\[link\]](#)).



Solutions of nonelectrolytes such as ethanol do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte.

Ionic Electrolytes

Water and other polar molecules are attracted to ions, as shown in [\[link\]](#). The electrostatic attraction between an ion and a molecule with a dipole is called an **ion-dipole attraction**. These attractions play an important role in the dissolution of ionic compounds in water.



As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown.

When ionic compounds dissolve in water, the ions in the solid separate and disperse uniformly throughout the solution because water molecules surround and solvate the ions, reducing the strong electrostatic forces between them. This process represents a physical change known as **dissociation**. Under most conditions, ionic compounds will dissociate

nearly completely when dissolved, and so they are classified as strong electrolytes.

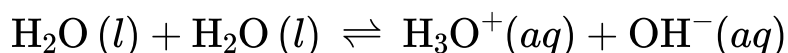
Let us consider what happens at the microscopic level when we add solid KCl to water. Ion-dipole forces attract the positive (hydrogen) end of the polar water molecules to the negative chloride ions at the surface of the solid, and they attract the negative (oxygen) ends to the positive potassium ions. The water molecules penetrate between individual K^+ and Cl^- ions and surround them, reducing the strong interionic forces that bind the ions together and letting them move off into solution as solvated ions, as [\[link\]](#) shows. The reduction of the electrostatic attraction permits the independent motion of each hydrated ion in a dilute solution, resulting in an increase in the disorder of the system as the ions change from their fixed and ordered positions in the crystal to mobile and much more disordered states in solution. This increased disorder is responsible for the dissolution of many ionic compounds, including KCl, which dissolve with absorption of heat.

In other cases, the electrostatic attractions between the ions in a crystal are so large, or the ion-dipole attractive forces between the ions and water molecules are so weak, that the increase in disorder cannot compensate for the energy required to separate the ions, and the crystal is insoluble. Such is the case for compounds such as calcium carbonate (limestone), calcium phosphate (the inorganic component of bone), and iron oxide (rust).

Covalent Electrolytes

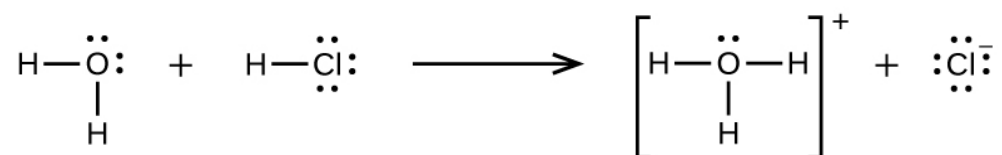
Pure water is an extremely poor conductor of electricity because it is only very slightly ionized—only about two out of every 1 billion molecules ionize at 25 °C. Water ionizes when one molecule of water gives up a proton (H^+ ion) to another molecule of water, yielding hydronium and hydroxide ions.

Equation:



In some cases, we find that solutions prepared from covalent compounds conduct electricity because the solute molecules react chemically with the solvent to produce ions. For example, pure hydrogen chloride is a gas consisting of covalent HCl molecules. This gas contains no ions. However, when we dissolve hydrogen chloride in water, we find that the solution is a very good conductor. The water molecules play an essential part in forming ions: Solutions of hydrogen chloride in many other solvents, such as benzene, do not conduct electricity and do not contain ions.

Hydrogen chloride is an *acid*, and so its molecules react with water, transferring H^+ ions to form hydronium ions (H_3O^+) and chloride ions (Cl^-):



This reaction is essentially 100% complete for HCl (i.e., it is a *strong acid* and, consequently, a strong electrolyte). Likewise, weak acids and bases that only react partially generate relatively low concentrations of ions when dissolved in water and are classified as weak electrolytes. The reader may wish to review the discussion of strong and weak acids provided in the earlier chapter of this text on reaction classes and stoichiometry.

Key Concepts and Summary

Substances that dissolve in water to yield ions are called electrolytes. Electrolytes may be covalent compounds that chemically react with water to produce ions (for example, acids and bases), or they may be ionic compounds that dissociate to yield their constituent cations and anions, when dissolved. Dissolution of an ionic compound is facilitated by ion-dipole attractions between the ions of the compound and the polar water molecules. Soluble ionic substances and strong acids ionize completely and are strong electrolytes, while weak acids and bases ionize to only a small extent and are weak electrolytes. Nonelectrolytes are substances that do not produce ions when dissolved in water.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Explain why the ions Na^+ and Cl^- are strongly solvated in water but not in hexane, a solvent composed of nonpolar molecules.

Solution:

Crystals of NaCl dissolve in water, a polar liquid with a very large dipole moment, and the individual ions become strongly solvated. Hexane is a nonpolar liquid with a dipole moment of zero and, therefore, does not significantly interact with the ions of the NaCl crystals.

Exercise:

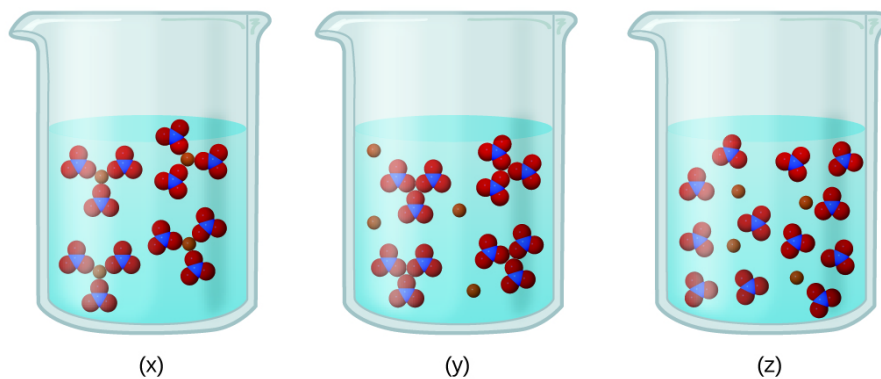
Problem:

Explain why solutions of HBr in benzene (a nonpolar solvent) are nonconductive, while solutions in water (a polar solvent) are conductive.

Exercise:

Problem: Consider the solutions presented:

(a) Which of the following sketches best represents the ions in a solution of $\text{Fe}(\text{NO}_3)_3(aq)$?



(b) Write a balanced chemical equation showing the products of the dissolution of $\text{Fe}(\text{NO}_3)_3$.

Solution:

(a) $\text{Fe}(\text{NO}_3)_3$ is a strong electrolyte, thus it should completely dissociate into Fe^{3+} and NO_3^- ions. Therefore, (z) best represents the solution. (b) $\text{Fe}(\text{NO}_3)_3(s) \longrightarrow \text{Fe}^{3+}(aq) + 3\text{NO}_3^-(aq)$

Exercise:

Problem:

Compare the processes that occur when methanol (CH_3OH), hydrogen chloride (HCl), and sodium hydroxide (NaOH) dissolve in water. Write equations and prepare sketches showing the form in which each of these compounds is present in its respective solution.

Exercise:

Problem:

What is the expected electrical conductivity of the following solutions?

- (a) $\text{NaOH}(aq)$
- (b) $\text{HCl}(aq)$
- (c) $\text{C}_6\text{H}_{12}\text{O}_6(aq)$ (glucose)
- (d) $\text{NH}_3(aq)$

Solution:

(a) high conductivity (solute is an ionic compound that will dissociate when dissolved); (b) high conductivity (solute is a strong acid and will ionize completely when dissolved); (c) nonconductive (solute is a covalent compound, neither acid nor base, unreactive towards water); (d) low conductivity (solute is a weak base and will partially ionize when dissolved)

Exercise:**Problem:**

Why are most *solid* ionic compounds electrically nonconductive, whereas aqueous solutions of ionic compounds are good conductors? Would you expect a *liquid* (molten) ionic compound to be electrically conductive or nonconductive? Explain.

Exercise:**Problem:**

Indicate the most important type of intermolecular attraction responsible for solvation in each of the following solutions:

- (a) the solutions in [\[link\]](#)
- (b) methanol, CH_3OH , dissolved in ethanol, $\text{C}_2\text{H}_5\text{OH}$
- (c) methane, CH_4 , dissolved in benzene, C_6H_6
- (d) the polar halocarbon CF_2Cl_2 dissolved in the polar halocarbon $\text{CF}_2\text{ClCFCl}_2$
- (e) $\text{O}_2(l)$ in $\text{N}_2(l)$

Solution:

(a) ion-dipole; (b) hydrogen bonds; (c) dispersion forces; (d) dipole-dipole attractions; (e) dispersion forces

Glossary

dissociation

physical process accompanying the dissolution of an ionic compound in which the compound's constituent ions are solvated and dispersed throughout the solution

electrolyte

substance that produces ions when dissolved in water

ion-dipole attraction

electrostatic attraction between an ion and a polar molecule

nonelectrolyte

substance that does not produce ions when dissolved in water

strong electrolyte

substance that dissociates or ionizes completely when dissolved in water

weak electrolyte

substance that ionizes only partially when dissolved in water

Solubility

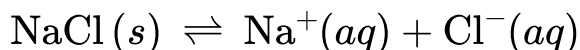
By the end of this module, you will be able to:

- Describe the effects of temperature and pressure on solubility
- State Henry's law and use it in calculations involving the solubility of a gas in a liquid
- Explain the degrees of solubility possible for liquid-liquid solutions

Imagine adding a small amount of salt to a glass of water, stirring until all the salt has dissolved, and then adding a bit more. You can repeat this process until the salt concentration of the solution reaches its natural limit, a limit determined primarily by the relative strengths of the solute-solute, solute-solvent, and solvent-solvent attractive forces discussed in the previous two modules of this chapter. You can be certain that you have reached this limit because, no matter how long you stir the solution, undissolved salt remains. The concentration of salt in the solution at this point is known as its solubility.

The **solubility** of a solute in a particular solvent is the maximum concentration that may be achieved under given conditions when the dissolution process is *at equilibrium*. Referring to the example of salt in water:

Equation:



When a solute's concentration is equal to its solubility, the solution is said to be **saturated** with that solute. If the solute's concentration is less than its solubility, the solution is said to be **unsaturated**. A solution that contains a relatively low concentration of solute is called dilute, and one with a relatively high concentration is called concentrated.

If we add more salt to a saturated solution of salt, we see it fall to the bottom and no more seems to dissolve. In fact, the added salt does dissolve, as represented by the forward direction of the dissolution equation. Accompanying this process, dissolved salt will precipitate, as depicted by the reverse direction of the equation. The system is said to be at equilibrium

when these two reciprocal processes are occurring at equal rates, and so the amount of undissolved and dissolved salt remains constant. Support for the simultaneous occurrence of the dissolution and precipitation processes is provided by noting that the number and sizes of the undissolved salt crystals will change over time, though their combined mass will remain the same.

Note:



Use this [interactive simulation](#) to prepare various saturated solutions.

Solutions may be prepared in which a solute concentration *exceeds* its solubility. Such solutions are said to be **supersaturated**, and they are interesting examples of *nonequilibrium* states. For example, the carbonated beverage in an open container that has not yet “gone flat” is supersaturated with carbon dioxide gas; given time, the CO_2 concentration will decrease until it reaches its equilibrium value.

Note:

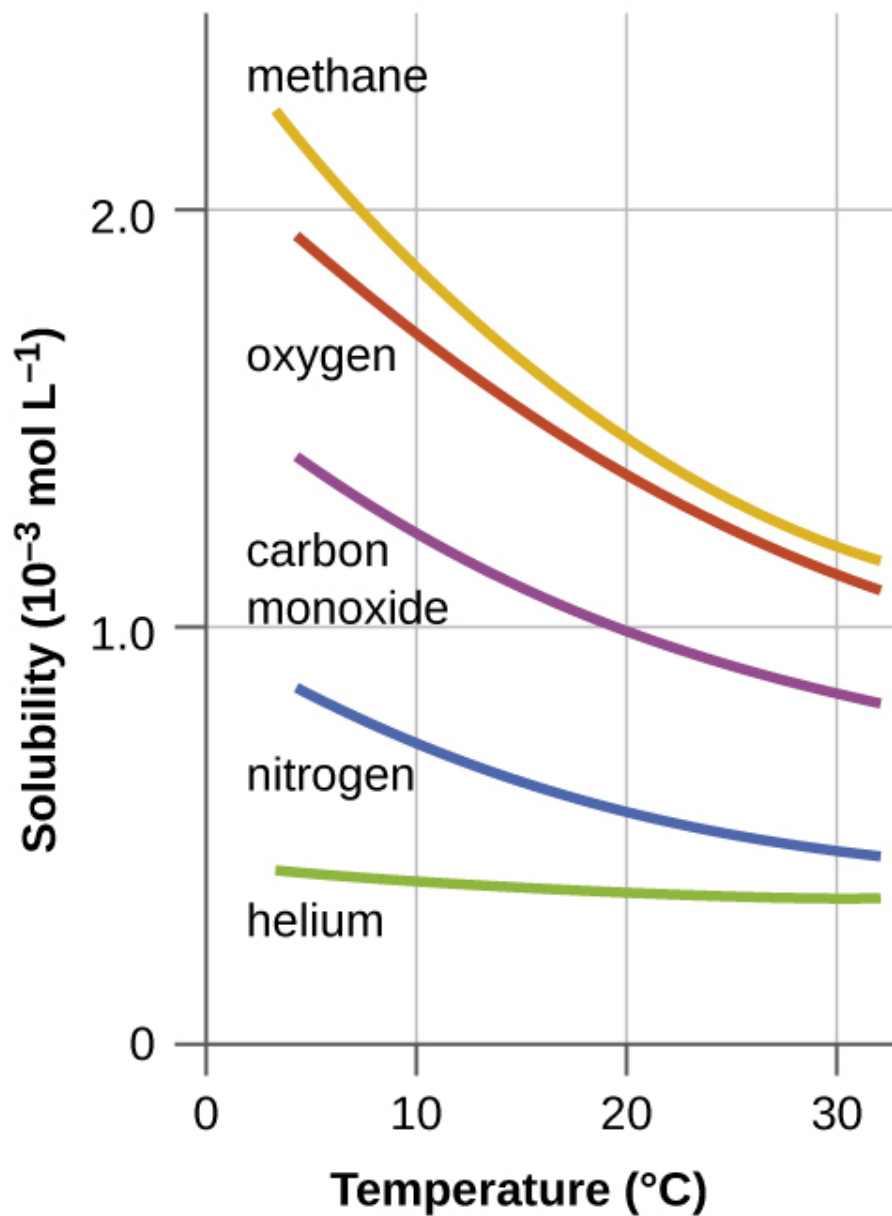


Watch this [impressive video](#) showing the precipitation of sodium acetate from a supersaturated solution.

Solutions of Gases in Liquids

In an earlier module of this chapter, the effect of intermolecular attractive forces on solution formation was discussed. The chemical structures of the solute and solvent dictate the types of forces possible and, consequently, are important factors in determining solubility. For example, under similar conditions, the water solubility of oxygen is approximately three times greater than that of helium, but 100 times less than the solubility of chloromethane, CHCl_3 . Considering the role of the solvent's chemical structure, note that the solubility of oxygen in the liquid hydrocarbon hexane, C_6H_{14} , is approximately 20 times greater than it is in water.

Other factors also affect the solubility of a given substance in a given solvent. Temperature is one such factor, with gas solubility typically decreasing as temperature increases ([link](#)). This is one of the major impacts resulting from the thermal pollution of natural bodies of water.



The solubilities of these gases in water decrease as the temperature increases. All solubilities were measured with a constant pressure of 101.3 kPa (1 atm) of gas above the solutions.

When the temperature of a river, lake, or stream is raised abnormally high, usually due to the discharge of hot water from some industrial process, the

solubility of oxygen in the water is decreased. Decreased levels of dissolved oxygen may have serious consequences for the health of the water's ecosystems and, in severe cases, can result in large-scale fish kills ([link](#)).



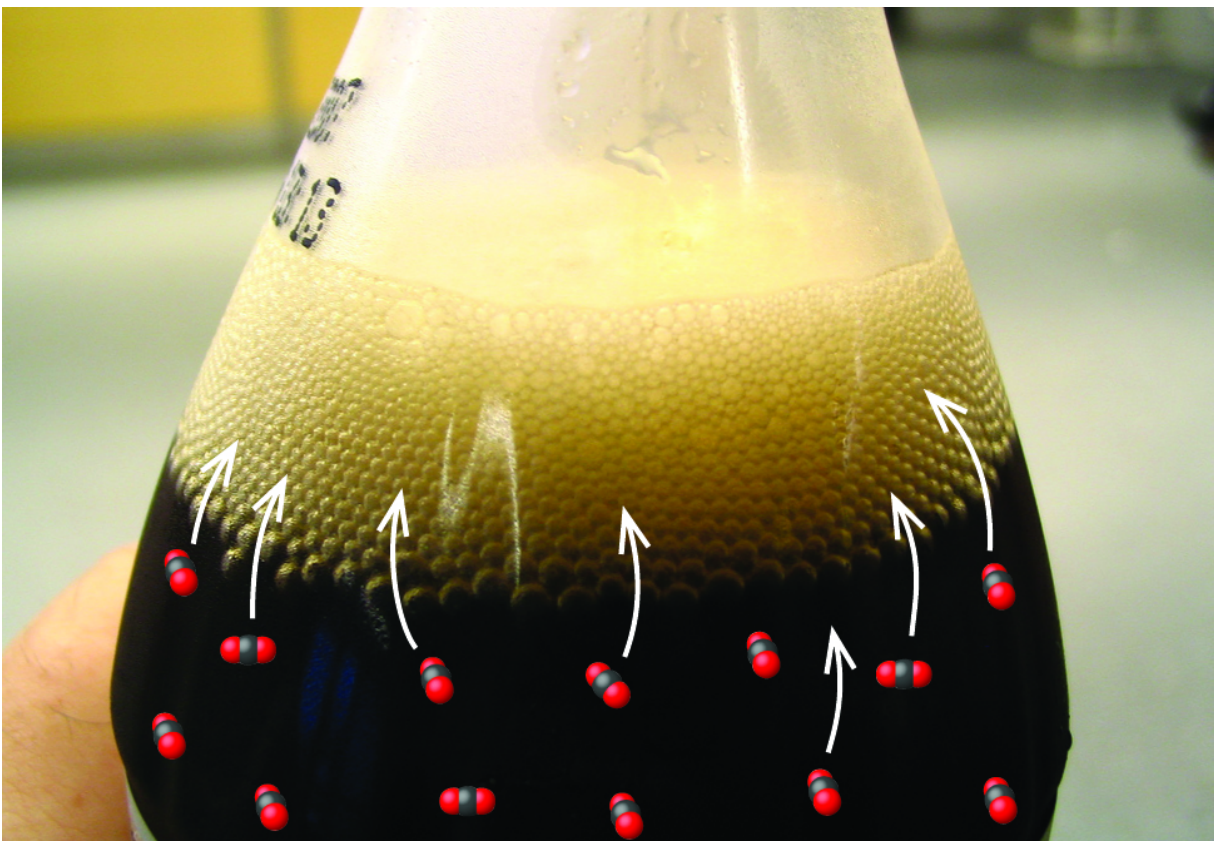
(a)



(b)

(a) The small bubbles of air in this glass of chilled water formed when the water warmed to room temperature and the solubility of its dissolved air decreased. (b) The decreased solubility of oxygen in natural waters subjected to thermal pollution can result in large-scale fish kills. (credit a: modification of work by Liz West; credit b: modification of work by U.S. Fish and Wildlife Service)

The solubility of a gaseous solute is also affected by the partial pressure of solute in the gas to which the solution is exposed. Gas solubility increases as the pressure of the gas increases. Carbonated beverages provide a nice illustration of this relationship. The carbonation process involves exposing the beverage to a relatively high pressure of carbon dioxide gas and then sealing the beverage container, thus saturating the beverage with CO_2 at this pressure. When the beverage container is opened, a familiar hiss is heard as the carbon dioxide gas pressure is released, and some of the dissolved carbon dioxide is typically seen leaving solution in the form of small bubbles ([link](#)). At this point, the beverage is *supersaturated* with carbon dioxide and, with time, the dissolved carbon dioxide concentration will decrease to its equilibrium value and the beverage will become “flat.”



Opening the bottle of carbonated beverage reduces the pressure of the *gaseous* carbon dioxide above the beverage. The solubility of CO₂ is thus lowered, and some *dissolved* carbon dioxide may be seen leaving the solution as small gas bubbles. (credit: modification of work by Derrick Coetzee)

For many gaseous solutes, the relation between solubility, C_g , and partial pressure, P_g , is a proportional one:

Equation:

$$C_g = kP_g$$

where k is a proportionality constant that depends on the identities of the gaseous solute and solvent, and on the solution temperature. This is a mathematical statement of **Henry's law**: *The quantity of an ideal gas that*

dissolves in a definite volume of liquid is directly proportional to the pressure of the gas.

Example:

Application of Henry's Law

At 20 °C, the concentration of dissolved oxygen in water exposed to gaseous oxygen at a partial pressure of 101.3 kPa (760 torr) is $1.38 \times 10^{-3} \text{ mol L}^{-1}$. Use Henry's law to determine the solubility of oxygen when its partial pressure is 20.7 kPa (155 torr), the approximate pressure of oxygen in earth's atmosphere.

Solution

According to Henry's law, for an ideal solution the solubility, C_g , of a gas ($1.38 \times 10^{-3} \text{ mol L}^{-1}$, in this case) is directly proportional to the pressure, P_g , of the undissolved gas above the solution (101.3 kPa, or 760 torr, in this case). Because we know both C_g and P_g , we can rearrange this expression to solve for k .

Equation:

$$\begin{aligned}C_g &= kP_g \\k &= \frac{C_g}{P_g} \\&= \frac{1.38 \times 10^{-3} \text{ mol L}^{-1}}{101.3 \text{ kPa}} \\&= 1.36 \times 10^{-5} \text{ mol L}^{-1} \text{ kPa}^{-1} \\&\quad (1.82 \times 10^{-6} \text{ mol L}^{-1} \text{ torr}^{-1})\end{aligned}$$

Now we can use k to find the solubility at the lower pressure.

Equation:

$$C_g = kP_g$$

Equation:

$$\begin{aligned}
 &1.36 \times 10^{-5} \text{ mol L}^{-1} \text{ kPa}^{-1} \times 20.7 \text{ kPa} \\
 &(\text{or } 1.82 \times 10^{-6} \text{ mol L}^{-1} \text{ torr}^{-1} \times 155 \text{ torr}) \\
 &= 2.82 \times 10^{-4} \text{ mol L}^{-1}
 \end{aligned}$$

Note that various units may be used to express the quantities involved in these sorts of computations. Any combination of units that yield to the constraints of dimensional analysis are acceptable.

Check Your Learning

Exposing a 100.0 mL sample of water at 0 °C to an atmosphere containing a gaseous solute at 20.26 kPa (152 torr) resulted in the dissolution of 1.45×10^{-3} g of the solute. Use Henry's law to determine the solubility of this gaseous solute when its pressure is 101.3 kPa (760 torr).

Note:

Answer:

7.25×10^{-3} in 100.0 mL or 0.0725 g/L

Note:

Decompression Sickness or “The Bends”

Decompression sickness (DCS), or “the bends,” is an effect of the increased pressure of the air inhaled by scuba divers when swimming underwater at considerable depths. In addition to the pressure exerted by the atmosphere, divers are subjected to additional pressure due to the water above them, experiencing an increase of approximately 1 atm for each 10 m of depth. Therefore, the air inhaled by a diver while submerged contains gases at the corresponding higher ambient pressure, and the concentrations of the gases dissolved in the diver's blood are proportionally higher per Henry's law.

As the diver ascends to the surface of the water, the ambient pressure decreases and the dissolved gases becomes less soluble. If the ascent is too

rapid, the gases escaping from the diver's blood may form bubbles that can cause a variety of symptoms ranging from rashes and joint pain to paralysis and death. To avoid DCS, divers must ascend from depths at relatively slow speeds (10 or 20 m/min) or otherwise make several decompression stops, pausing for several minutes at given depths during the ascent. When these preventive measures are unsuccessful, divers with DCS are often provided hyperbaric oxygen therapy in pressurized vessels called decompression (or recompression) chambers ([\[link\]](#)).



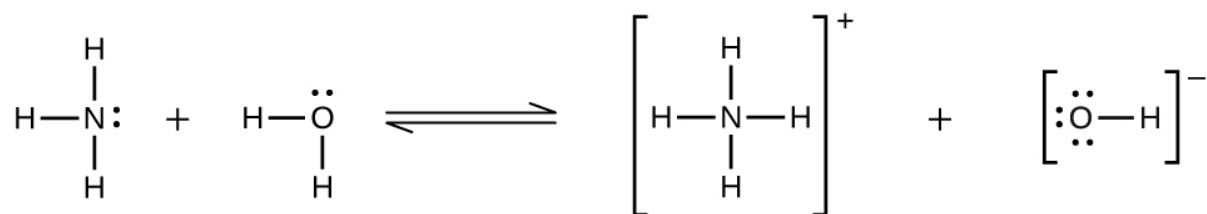
(a)



(b)

(a) US Navy divers undergo training in a recompression chamber. (b) Divers receive hyperbaric oxygen therapy.

Deviations from Henry's law are observed when a chemical reaction takes place between the gaseous solute and the solvent. Thus, for example, the solubility of ammonia in water does not increase as rapidly with increasing pressure as predicted by the law because ammonia, being a base, reacts to some extent with water to form ammonium ions and hydroxide ions.



Gases can form supersaturated solutions. If a solution of a gas in a liquid is prepared either at low temperature or under pressure (or both), then as the solution warms or as the gas pressure is reduced, the solution may become supersaturated. In 1986, more than 1700 people in Cameroon were killed when a cloud of gas, almost certainly carbon dioxide, bubbled from Lake Nyos ([link](#)), a deep lake in a volcanic crater. The water at the bottom of Lake Nyos is saturated with carbon dioxide by volcanic activity beneath the lake. It is believed that the lake underwent a turnover due to gradual heating from below the lake, and the warmer, less-dense water saturated with carbon dioxide reached the surface. Consequently, tremendous quantities of dissolved CO₂ were released, and the colorless gas, which is denser than air, flowed down the valley below the lake and suffocated humans and animals living in the valley.



(a)



(b)

(a) It is believed that the 1986 disaster that killed more than 1700 people near Lake Nyos in Cameroon resulted when a large volume of carbon dioxide gas was released from the lake. (b) A CO₂ vent has since been installed to help outgas the lake in a slow, controlled fashion and prevent a similar catastrophe from happening in the future.

(credit a: modification of work by Jack Lockwood; credit b:
modification of work by Bill Evans)

Solutions of Liquids in Liquids

We know that some liquids mix with each other in all proportions; in other words, they have infinite mutual solubility and are said to be **miscible**.

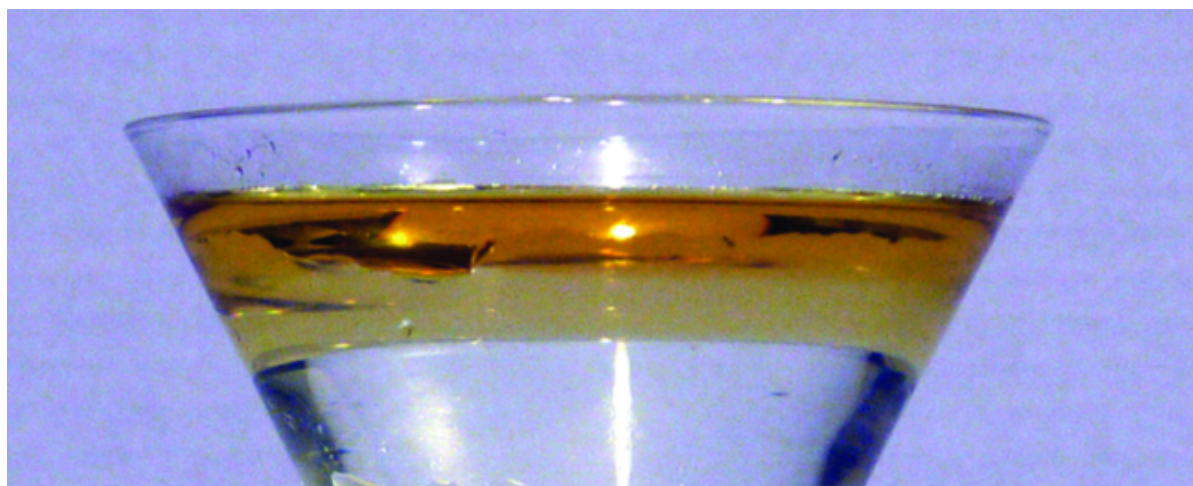
Ethanol, sulfuric acid, and ethylene glycol (popular for use as antifreeze, pictured in [\[link\]](#)) are examples of liquids that are completely miscible with water. Two-cycle motor oil is miscible with gasoline.



Water and antifreeze are miscible; mixtures of the two are homogeneous in all proportions. (credit: “dno1967”/Wikimedia commons)

Liquids that mix with water in all proportions are usually polar substances or substances that form hydrogen bonds. For such liquids, the dipole-dipole attractions (or hydrogen bonding) of the solute molecules with the solvent molecules are at least as strong as those between molecules in the pure solute or in the pure solvent. Hence, the two kinds of molecules mix easily. Likewise, nonpolar liquids are miscible with each other because there is no appreciable difference in the strengths of solute-solute, solvent-solvent, and solute-solvent intermolecular attractions. The solubility of polar molecules in polar solvents and of nonpolar molecules in nonpolar solvents is, again, an illustration of the chemical axiom “like dissolves like.”

Two liquids that do not mix to an appreciable extent are called **immiscible**. Layers are formed when we pour immiscible liquids into the same container. Gasoline, oil ([\[link\]](#)), benzene, carbon tetrachloride, some paints, and many other nonpolar liquids are immiscible with water. The attraction between the molecules of such nonpolar liquids and polar water molecules is ineffectively weak. The only strong attractions in such a mixture are between the water molecules, so they effectively squeeze out the molecules of the nonpolar liquid. The distinction between immiscibility and miscibility is really one of degrees, so that miscible liquids are of infinite mutual solubility, while liquids said to be immiscible are of very low (though not zero) mutual solubility.





Water and oil are immiscible. Mixtures of these two substances will form two separate layers with the less dense oil floating on top of the water. (credit: “Yortw”/Flickr)

Two liquids, such as bromine and water, that are of *moderate* mutual solubility are said to be **partially miscible**. Two partially miscible liquids usually form two layers when mixed. In the case of the bromine and water

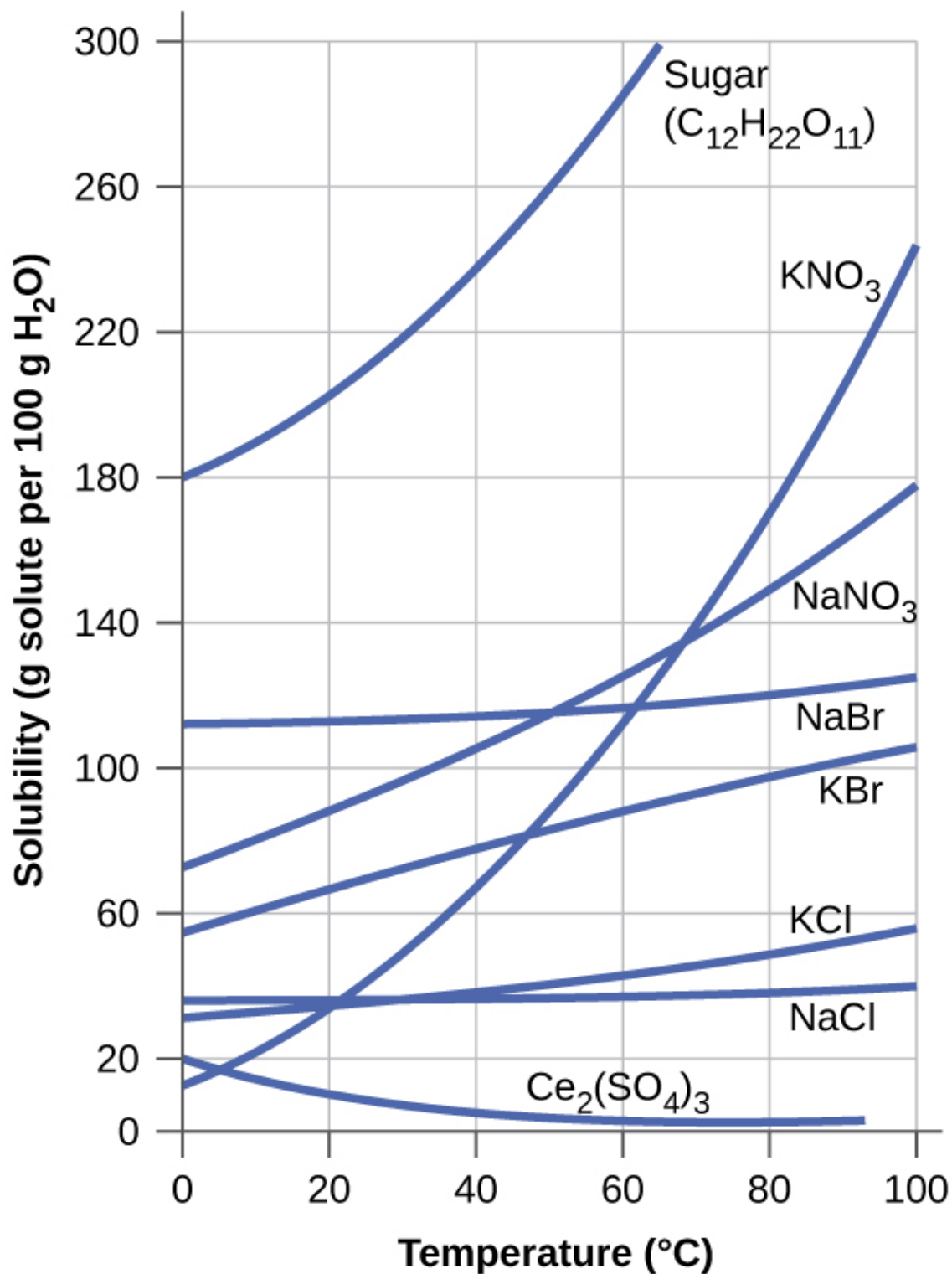
mixture, the upper layer is water, saturated with bromine, and the lower layer is bromine saturated with water. Since bromine is nonpolar, and, thus, not very soluble in water, the water layer is only slightly discolored by the bright orange bromine dissolved in it. Since the solubility of water in bromine is very low, there is no noticeable effect on the dark color of the bromine layer ([link](#)).



Bromine (the deep orange liquid on the left) and water (the clear liquid in the middle) are partially miscible. The top layer in the mixture on the right is a saturated solution of bromine in water; the bottom layer is a saturated solution of water in bromine. (credit: Paul Flowers)

Solutions of Solids in Liquids

The dependence of solubility on temperature for a number of solids in water is shown by the solubility curves in [\[link\]](#). Reviewing these data indicate a general trend of increasing solubility with temperature, although there are exceptions, as illustrated by the ionic compound cerium sulfate.



This graph shows how the solubility of several solids changes with temperature.

The temperature dependence of solubility can be exploited to prepare supersaturated solutions of certain compounds. A solution may be saturated with the compound at an elevated temperature (where the solute is more soluble) and subsequently cooled to a lower temperature without precipitating the solute. The resultant solution contains solute at a concentration greater than its equilibrium solubility at the lower temperature (i.e., it is supersaturated) and is relatively stable. Precipitation of the excess solute can be initiated by adding a seed crystal (see the video in the Link to Learning earlier in this module) or by mechanically agitating the solution. Some hand warmers, such as the one pictured in [\[link\]](#), take advantage of this behavior.



This hand warmer produces heat when the sodium acetate in a supersaturated solution precipitates. Precipitation of the solute is initiated by a mechanical shockwave generated when the flexible metal disk within the solution is “clicked.” (credit: modification of work by “Velela”/Wikimedia Commons)

Note:



This [video](#) shows the crystallization process occurring in a hand warmer.

Key Concepts and Summary

The extent to which one substance will dissolve in another is determined by several factors, including the types and relative strengths of intermolecular attractive forces that may exist between the substances' atoms, ions, or molecules. This tendency to dissolve is quantified as a substance's solubility, its maximum concentration in a solution at equilibrium under specified conditions. A saturated solution contains solute at a concentration equal to its solubility. A supersaturated solution is one in which a solute's concentration exceeds its solubility—a nonequilibrium (unstable) condition that will result in solute precipitation when the solution is appropriately perturbed. Miscible liquids are soluble in all proportions, and immiscible liquids exhibit very low mutual solubility. Solubilities for gaseous solutes decrease with increasing temperature, while those for most, but not all, solid solutes increase with temperature. The concentration of a gaseous solute in a solution is proportional to the partial pressure of the gas to which the solution is exposed, a relation known as Henry's law.

Key Equations

- $C_g = kP_g$

Chemistry End of Chapter Exercises

Exercise:

Problem:

Suppose you are presented with a clear solution of sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$. How could you determine whether the solution is unsaturated, saturated, or supersaturated?

Exercise:**Problem:**

Supersaturated solutions of most solids in water are prepared by cooling saturated solutions. Supersaturated solutions of most gases in water are prepared by heating saturated solutions. Explain the reasons for the difference in the two procedures.

Solution:

The solubility of solids usually decreases upon cooling a solution, while the solubility of gases usually decreases upon heating.

Exercise:**Problem:**

Suggest an explanation for the observations that ethanol, $\text{C}_2\text{H}_5\text{OH}$, is completely miscible with water and that ethanethiol, $\text{C}_2\text{H}_5\text{SH}$, is soluble only to the extent of 1.5 g per 100 mL of water.

Exercise:**Problem:**

Calculate the percent by mass of KBr in a saturated solution of KBr in water at 10 °C. See [\[link\]](#) for useful data, and report the computed percentage to one significant digit.

Solution:

40%

Exercise:

Problem:

Which of the following gases is expected to be most soluble in water? Explain your reasoning.

- (a) CH_4
- (b) CCl_4
- (c) CHCl_3

Exercise:**Problem:**

At 0 °C and 1.00 atm, as much as 0.70 g of O_2 can dissolve in 1 L of water. At 0 °C and 4.00 atm, how many grams of O_2 dissolve in 1 L of water?

Solution:

2.8 g

Exercise:

Problem: Refer to [\[link\]](#).

- (a) How did the concentration of dissolved CO_2 in the beverage change when the bottle was opened?
- (b) What caused this change?
- (c) Is the beverage unsaturated, saturated, or supersaturated with CO_2 ?

Exercise:

Problem:

The Henry's law constant for CO_2 is $3.4 \times 10^{-2} \text{ M/atm}$ at 25°C . What pressure of carbon dioxide is needed to maintain a CO_2 concentration of 0.10 M in a can of lemon-lime soda?

Solution:

2.9 atm

Exercise:**Problem:**

The Henry's law constant for O_2 is $1.3 \times 10^{-3} \text{ M/atm}$ at 25°C . What mass of oxygen would be dissolved in a 40-L aquarium at 25°C , assuming an atmospheric pressure of 1.00 atm, and that the partial pressure of O_2 is 0.21 atm?

Exercise:**Problem:**

How many liters of HCl gas, measured at 30.0°C and 745 torr, are required to prepare 1.25 L of a 3.20-M solution of hydrochloric acid?

Solution:

102 L HCl

Glossary**Henry's law**

law stating the proportional relationship between the concentration of dissolved gas in a solution and the partial pressure of the gas in contact with the solution

immiscible

of negligible mutual solubility; typically refers to liquid substances

miscible

mutually soluble in all proportions; typically refers to liquid substances

partially miscible

of moderate mutual solubility; typically refers to liquid substances

saturated

of concentration equal to solubility; containing the maximum concentration of solute possible for a given temperature and pressure

solubility

extent to which a solute may be dissolved in water, or any solvent

supersaturated

of concentration that exceeds solubility; a nonequilibrium state

unsaturated

of concentration less than solubility

Colligative Properties

By the end of this section, you will be able to:

- Express concentrations of solution components using mole fraction and molality
- Describe the effect of solute concentration on various solution properties (vapor pressure, boiling point, freezing point, and osmotic pressure)
- Perform calculations using the mathematical equations that describe these various colligative effects
- Describe the process of distillation and its practical applications
- Explain the process of osmosis and describe how it is applied industrially and in nature

The properties of a solution are different from those of either the pure solute(s) or solvent. Many solution properties are dependent upon the chemical identity of the solute. Compared to pure water, a solution of hydrogen chloride is more acidic, a solution of ammonia is more basic, a solution of sodium chloride is more dense, and a solution of sucrose is more viscous. There are a few solution properties, however, that depend *only* upon the total concentration of solute species, regardless of their identities. These **colligative properties** include vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. This small set of properties is of central importance to many natural phenomena and technological applications, as will be described in this module.

Mole Fraction and Molality

Several units commonly used to express the concentrations of solution components were introduced in an earlier chapter of this text, each providing certain benefits for use in different applications. For example, molarity (M) is a convenient unit for use in stoichiometric calculations, since it is defined in terms of the molar amounts of solute species:

Equation:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

Because solution volumes vary with temperature, molar concentrations will likewise vary. When expressed as molarity, the concentration of a solution with identical numbers of solute and solvent species will be different at different temperatures, due to the contraction/expansion of the solution. More appropriate for calculations involving many colligative properties are mole-based concentration units whose values are not dependent on temperature. Two such units are *mole fraction* (introduced in the previous chapter on gases) and *molality*.

The mole fraction, X , of a component is the ratio of its molar amount to the total number of moles of all solution components:

Equation:

$$X_A = \frac{\text{mol A}}{\text{total mol of all components}}$$

Molality is a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms:

Equation:

$$m = \frac{\text{mol solute}}{\text{kg solvent}}$$

Since these units are computed using only masses and molar amounts, they do not vary with temperature and, thus, are better suited for applications requiring temperature-independent concentrations, including several colligative properties, as will be described in this chapter module.

Example:

Calculating Mole Fraction and Molality

The antifreeze in most automobile radiators is a mixture of equal volumes of ethylene glycol and water, with minor amounts of other additives that prevent corrosion. What are the (a) mole fraction and (b) molality of ethylene glycol, $\text{C}_2\text{H}_4(\text{OH})_2$, in a solution prepared from $2.22 \times 10^3 \text{ g}$ of ethylene glycol and $2.00 \times 10^3 \text{ g}$ of water (approximately 2 L of glycol and 2 L of water)?

Solution

(a) The mole fraction of ethylene glycol may be computed by first deriving molar amounts of both solution components and then substituting these amounts into the unit definition.

Equation:

$$\begin{aligned}\text{mol C}_2\text{H}_4(\text{OH})_2 &= 2.22 \times 10^3 \text{ g} \times \frac{1 \text{ mol C}_2\text{H}_4(\text{OH})_2}{62.07 \text{ g C}_2\text{H}_4(\text{OH})_2} = 35.8 \text{ mol C}_2\text{H}_4(\text{OH})_2 \\ \text{mol H}_2\text{O} &= 2.00 \times 10^3 \text{ g} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 111 \text{ mol H}_2\text{O} \\ X_{\text{ethylene glycol}} &= \frac{35.8 \text{ mol C}_2\text{H}_4(\text{OH})_2}{(35.8 + 111) \text{ mol total}} = 0.244\end{aligned}$$

Notice that mole fraction is a dimensionless property, being the ratio of properties with identical units (moles).

(b) To find molality, we need to know the moles of the solute and the mass of the solvent (in kg). First, use the given mass of ethylene glycol and its molar mass to find the moles of solute:

Equation:

$$2.22 \times 10^3 \text{ g C}_2\text{H}_4(\text{OH})_2 \left(\frac{1 \text{ mol C}_2\text{H}_4(\text{OH})_2}{62.07 \text{ g}} \right) = 35.8 \text{ mol C}_2\text{H}_4(\text{OH})_2$$

Then, convert the mass of the water from grams to kilograms:

Equation:

$$2.00 \times 10^3 \text{ g H}_2\text{O} \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 2.00 \text{ kg H}_2\text{O}$$

Finally, calculate molality per its definition:

Equation:

$$\begin{aligned}\text{molality} &= \frac{\text{mol solute}}{\text{kg solvent}} \\ \text{molality} &= \frac{35.8 \text{ mol C}_2\text{H}_4(\text{OH})_2}{2 \text{ kg H}_2\text{O}} \\ \text{molality} &= 17.9 \text{ m}\end{aligned}$$

Check Your Learning

What are the mole fraction and molality of a solution that contains 0.850 g of ammonia, NH_3 , dissolved in 125 g of water?

Note:

Answer:

7.14×10^{-3} ; 0.399 *m*

Example:**Converting Mole Fraction and Molal Concentrations**

Calculate the mole fraction of solute and solvent in a 3.0 *m* solution of sodium chloride.

Solution

Converting from one concentration unit to another is accomplished by first comparing the two unit definitions. In this case, both units have the same numerator (moles of solute) but different denominators. The provided molal concentration may be written as:

Equation:

$$\frac{3.0 \text{ mol NaCl}}{1.0 \text{ kg H}_2\text{O}}$$

The numerator for this solution's mole fraction is, therefore, 3.0 mol NaCl. The denominator may be computed by deriving the molar amount of water corresponding to 1.0 kg

Equation:

$$1.0 \text{ kg H}_2\text{O} \left(\frac{1000 \text{ g}}{1 \text{ kg}} \right) \left(\frac{\text{mol H}_2\text{O}}{18.02 \text{ g}} \right) = 55 \text{ mol H}_2\text{O}$$

and then substituting these molar amounts into the definition for mole fraction.

Equation:

$$\begin{aligned} X_{\text{H}_2\text{O}} &= \frac{\text{mol H}_2\text{O}}{\text{mol NaCl} + \text{mol H}_2\text{O}} \\ X_{\text{H}_2\text{O}} &= \frac{55 \text{ mol H}_2\text{O}}{3.0 \text{ mol NaCl} + 55 \text{ mol H}_2\text{O}} \\ X_{\text{H}_2\text{O}} &= 0.95 \\ X_{\text{NaCl}} &= \frac{\text{mol NaCl}}{\text{mol NaCl} + \text{mol H}_2\text{O}} \\ X_{\text{NaCl}} &= \frac{3.0 \text{ mol NaCl}}{3.0 \text{ mol NaCl} + 55 \text{ mol H}_2\text{O}} \\ X_{\text{NaCl}} &= 0.052 \end{aligned}$$

Check Your Learning

The mole fraction of iodine, I_2 , dissolved in dichloromethane, CH_2Cl_2 , is 0.115. What is the molal concentration, *m*, of iodine in this solution?

Note:

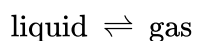
Answer:

1.50 m

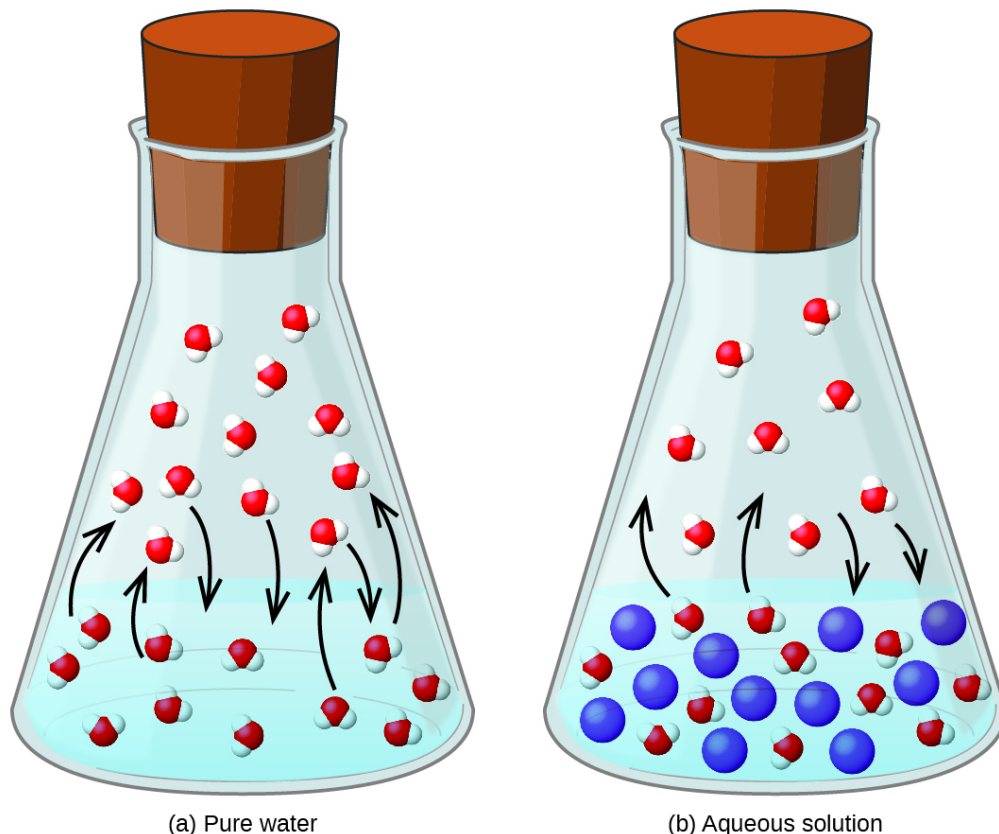
Vapor Pressure Lowering

As described in the chapter on liquids and solids, the equilibrium vapor pressure of a liquid is the pressure exerted by its gaseous phase when vaporization and condensation are occurring at equal rates:

Equation:



Dissolving a nonvolatile substance in a volatile liquid results in a lowering of the liquid's vapor pressure. This phenomenon can be rationalized by considering the effect of added solute molecules on the liquid's vaporization and condensation processes. To vaporize, solvent molecules must be present at the surface of the solution. The presence of solute decreases the surface area available to solvent molecules and thereby reduces the rate of solvent vaporization. Since the rate of condensation is unaffected by the presence of solute, the net result is that the vaporization-condensation equilibrium is achieved with fewer solvent molecules in the vapor phase (i.e., at a lower vapor pressure) ([link](#)). While this kinetic interpretation is useful, it does not account for several important aspects of the colligative nature of vapor pressure lowering. A more rigorous explanation involves the property of *entropy*, a topic of discussion in a later text chapter on thermodynamics. For purposes of understanding the lowering of a liquid's vapor pressure, it is adequate to note that the greater entropy of a solution in comparison to its separate solvent and solute serves to effectively stabilize the solvent molecules and hinder their vaporization. A lower vapor pressure results, and a correspondingly higher boiling point as described in the next section of this module.



The presence of nonvolatile solutes lowers the vapor pressure of a solution by impeding the evaporation of solvent molecules.

The relationship between the vapor pressures of solution components and the concentrations of those components is described by **Raoult's law**: *The partial pressure exerted by any component of an ideal solution is equal to the vapor pressure of the pure component multiplied by its mole fraction in the solution.*

Equation:

$$P_A = X_A P_A^\circ$$

where P_A is the partial pressure exerted by component A in the solution, P_A° is the vapor pressure of pure A, and X_A is the mole fraction of A in the solution. (Mole fraction is a concentration unit introduced in the chapter on gases.)

Recalling that the total pressure of a gaseous mixture is equal to the sum of partial pressures for all its components (Dalton's law of partial pressures), the total vapor pressure exerted by a solution containing i components is

Equation:

$$P_{\text{solution}} = \sum_i P_i = \sum_i X_i P_i^{\circ}$$

A nonvolatile substance is one whose vapor pressure is negligible ($P^{\circ} \approx 0$), and so the vapor pressure above a solution containing only nonvolatile solutes is due only to the solvent:

Equation:

$$P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^{\circ}$$

Example:

Calculation of a Vapor Pressure

Compute the vapor pressure of an ideal solution containing 92.1 g of glycerin, $\text{C}_3\text{H}_5(\text{OH})_3$, and 184.4 g of ethanol, $\text{C}_2\text{H}_5\text{OH}$, at 40 °C. The vapor pressure of pure ethanol is 0.178 atm at 40 °C. Glycerin is essentially nonvolatile at this temperature.

Solution

Since the solvent is the only volatile component of this solution, its vapor pressure may be computed per Raoult's law as:

Equation:

$$P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^{\circ}$$

First, calculate the molar amounts of each solution component using the provided mass data.

Equation:

$$92.1 \text{ g } \text{C}_3\text{H}_5(\text{OH})_3 \times \frac{1 \text{ mol } \text{C}_3\text{H}_5(\text{OH})_3}{92.094 \text{ g } \text{C}_3\text{H}_5(\text{OH})_3} = 1.00 \text{ mol } \text{C}_3\text{H}_5(\text{OH})_3$$

$$184.4 \text{ g } \text{C}_2\text{H}_5\text{OH} \times \frac{1 \text{ mol } \text{C}_2\text{H}_5\text{OH}}{46.069 \text{ g } \text{C}_2\text{H}_5\text{OH}} = 4.000 \text{ mol } \text{C}_2\text{H}_5\text{OH}$$

Next, calculate the mole fraction of the solvent (ethanol) and use Raoult's law to compute the solution's vapor pressure.

Equation:

$$X_{\text{C}_2\text{H}_5\text{OH}} = \frac{4.000 \text{ mol}}{(1.00 \text{ mol} + 4.000 \text{ mol})} = 0.800$$

$$P_{\text{solv}} = X_{\text{solv}} P_{\text{solv}}^{\circ} = 0.800 \times 0.178 \text{ atm} = 0.142 \text{ atm}$$

Check Your Learning

A solution contains 5.00 g of urea, $\text{CO}(\text{NH}_2)_2$ (a nonvolatile solute) and 0.100 kg of water. If the vapor pressure of pure water at 25 °C is 23.7 torr, what is the vapor pressure of the solution?

Note:

Answer:

23.4 torr

Elevation of the Boiling Point of a Solvent

As described in the chapter on liquids and solids, the *boiling point* of a liquid is the temperature at which its vapor pressure is equal to ambient atmospheric pressure. Since the vapor pressure of a solution is lowered due to the presence of nonvolatile solutes, it stands to reason that the solution's boiling point will subsequently be increased. Compared to pure solvent, a solution, therefore, will require a higher temperature to achieve any given vapor pressure, including one equivalent to that of the surrounding atmosphere. The increase in boiling point observed when nonvolatile solute is dissolved in a solvent, ΔT_b , is called **boiling point elevation** and is directly proportional to the molal concentration of solute species:

Equation:

$$\Delta T_b = K_b m$$

where K_b is the **boiling point elevation constant**, or the *ebullioscopic constant* and m is the molal concentration (molality) of all solute species.

Boiling point elevation constants are characteristic properties that depend on the identity of the solvent. Values of K_b for several solvents are listed in [\[link\]](#).

Boiling Point Elevation and Freezing Point Depression Constants for Several Solvents				
Solvent	Boiling Point (°C at 1 atm)	K_b (°C m^{-1})	Freezing Point (°C at 1 atm)	K_f (°C m^{-1})
water	100.0	0.512	0.0	1.86
hydrogen acetate	118.1	3.07	16.6	3.9
benzene	80.1	2.53	5.5	5.12
chloroform	61.26	3.63	−63.5	4.68
nitrobenzene	210.9	5.24	5.67	8.1

The extent to which the vapor pressure of a solvent is lowered and the boiling point is elevated depends on the total number of solute particles present in a given amount of solvent, not on the mass or size or chemical identities of the particles. A 1 m aqueous solution of sucrose (342 g/mol) and a 1

m aqueous solution of ethylene glycol (62 g/mol) will exhibit the same boiling point because each solution has one mole of solute particles (molecules) per kilogram of solvent.

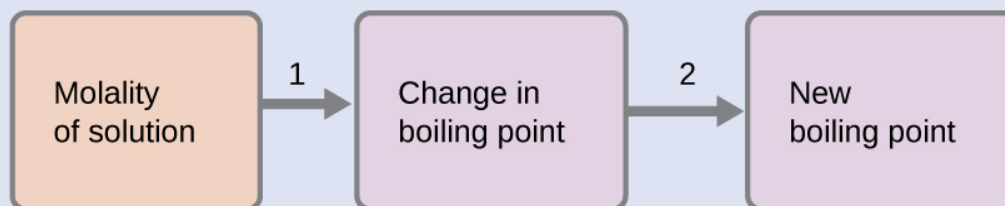
Example:

Calculating the Boiling Point of a Solution

What is the boiling point of a 0.33 m solution of a nonvolatile solute in benzene?

Solution

Use the equation relating boiling point elevation to solute molality to solve this problem in two steps.



Calculate the change in boiling point. **Equation:**

$$\Delta T_b = K_b m = 2.53\text{ }^{\circ}\text{C } m^{-1} \times 0.33\text{ } m = 0.83\text{ }^{\circ}\text{C}$$

Add the boiling point elevation to the pure solvent's boiling point. **Equation:**

$$\text{Boiling temperature} = 80.1\text{ }^{\circ}\text{C} + 0.83\text{ }^{\circ}\text{C} = 80.9\text{ }^{\circ}\text{C}$$

Check Your Learning

What is the boiling point of the antifreeze described in [\[link\]](#)?

Note:

Answer:

109.2 $^{\circ}\text{C}$

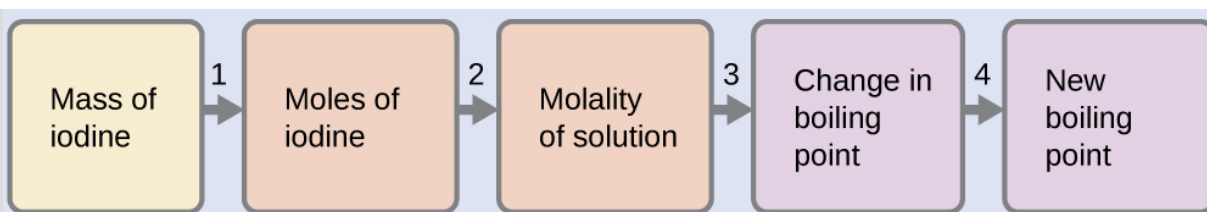
Example:

The Boiling Point of an Iodine Solution

Find the boiling point of a solution of 92.1 g of iodine, I_2 , in 800.0 g of chloroform, CHCl_3 , assuming that the iodine is nonvolatile and that the solution is ideal.

Solution

We can solve this problem using four steps.



Convert from grams to moles I_2 using the molar mass of I_2 in the unit conversion of factor. Result: 0.363 mol

Determine the molality of the solution from the number of moles of solute and the mass of solvent, in kilograms. Result: 0.454 m

Use the direct proportionality between the change in boiling point and molal concentration to determine how much the boiling point changes. Result: 1.65 °C

Determine the new boiling point from the boiling point of the pure solvent and the change. Result: 62.91 °C Check each result as a self-assessment.

Check Your Learning

What is the boiling point of a solution of 1.0 g of glycerin, $C_3H_5(OH)_3$, in 47.8 g of water? Assume an ideal solution.

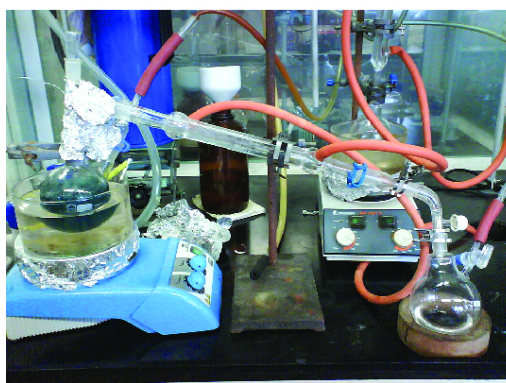
Note:

Answer:

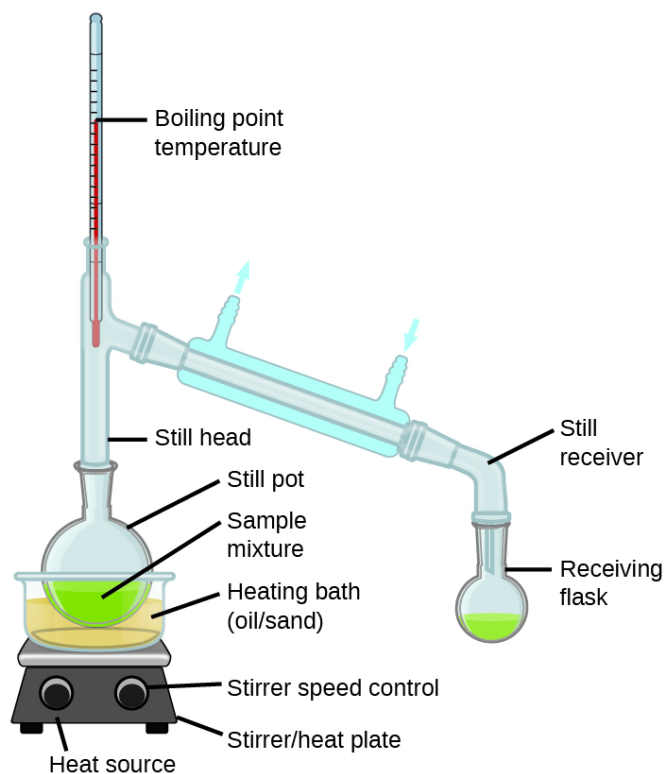
100.12 °C

Distillation of Solutions

Distillation is a technique for separating the components of mixtures that is widely applied in both in the laboratory and in industrial settings. It is used to refine petroleum, to isolate fermentation products, and to purify water. This separation technique involves the controlled heating of a sample mixture to selectively vaporize, condense, and collect one or more components of interest. A typical apparatus for laboratory-scale distillations is shown in [\[link\]](#).



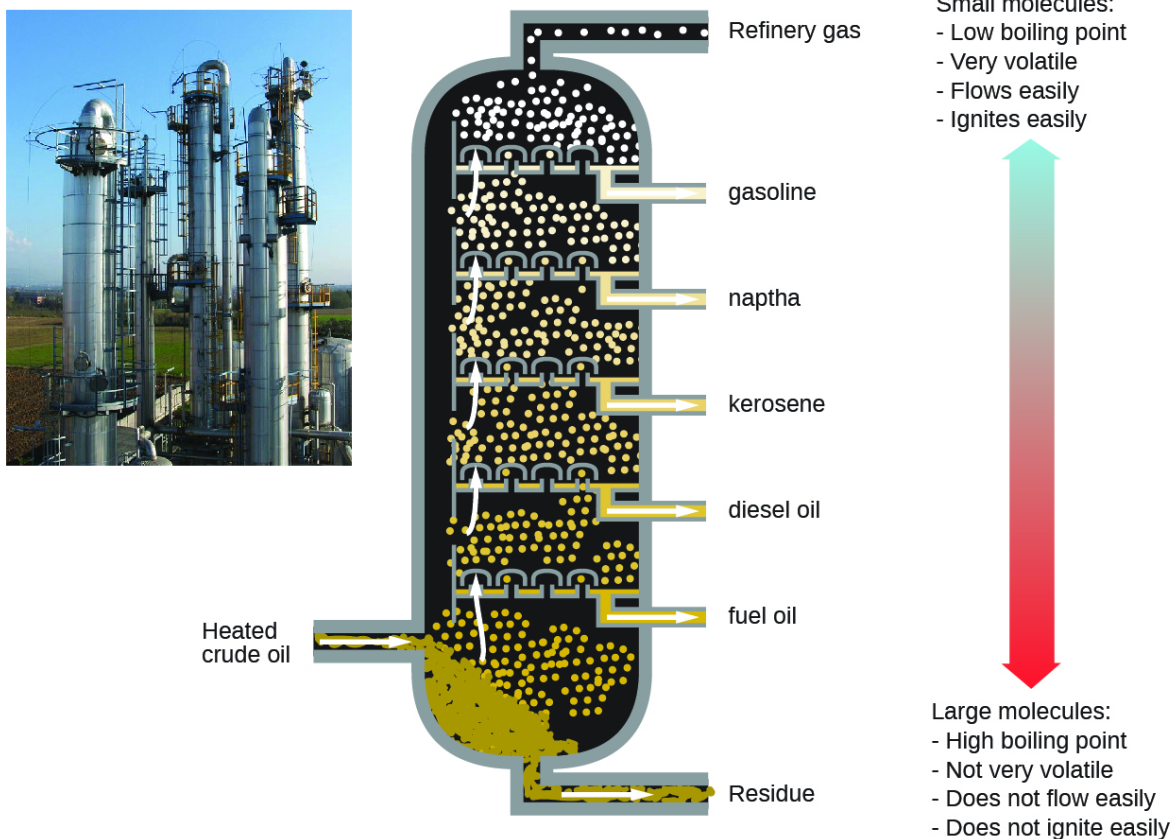
(a)



(b)

A typical laboratory distillation unit is shown in (a) a photograph and (b) a schematic diagram of the components. (credit a: modification of work by “Rifleman82”/Wikimedia commons; credit b: modification of work by “Slashme”/Wikimedia Commons)

Oil refineries use large-scale *fractional distillation* to separate the components of crude oil. The crude oil is heated to high temperatures at the base of a tall *fractionating column*, vaporizing many of the components that rise within the column. As vaporized components reach adequately cool zones during their ascent, they condense and are collected. The collected liquids are simpler mixtures of hydrocarbons and other petroleum compounds that are of appropriate composition for various applications (e.g., diesel fuel, kerosene, gasoline), as depicted in [\[link\]](#).



Crude oil is a complex mixture that is separated by large-scale fractional distillation to isolate various simpler mixtures.

Depression of the Freezing Point of a Solvent

Solutions freeze at lower temperatures than pure liquids. This phenomenon is exploited in “de-icing” schemes that use salt ([link](#)), calcium chloride, or urea to melt ice on roads and sidewalks, and in the use of ethylene glycol as an “antifreeze” in automobile radiators. Seawater freezes at a lower temperature than fresh water, and so the Arctic and Antarctic oceans remain unfrozen even at temperatures below 0 °C (as do the body fluids of fish and other cold-blooded sea animals that live in these oceans).



Rock salt (NaCl), calcium chloride (CaCl₂), or a mixture of the two are used to melt ice. (credit: modification of work by Eddie Welker)

The decrease in freezing point of a dilute solution compared to that of the pure solvent, ΔT_f , is called the **freezing point depression** and is directly proportional to the molal concentration of the solute
Equation:

$$\Delta T_f = K_f m$$

where m is the molal concentration of the solute and K_f is called the **freezing point depression constant** (or *cryoscopic constant*). Just as for boiling point elevation constants, these are characteristic properties whose values depend on the chemical identity of the solvent. Values of K_f for several solvents are listed in [\[link\]](#).

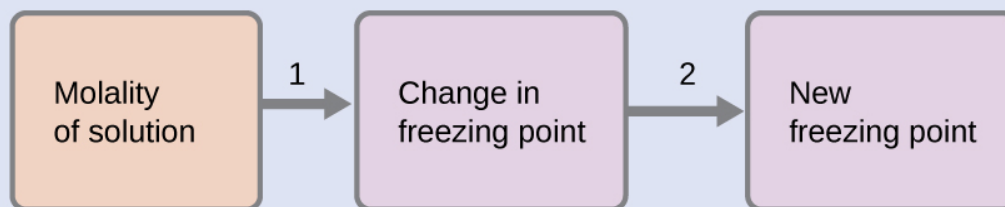
Example:

Calculation of the Freezing Point of a Solution

What is the freezing point of the 0.33 m solution of a nonvolatile nonelectrolyte solute in benzene described in [\[link\]](#)?

Solution

Use the equation relating freezing point depression to solute molality to solve this problem in two steps.



Calculate the change in freezing point. **Equation:**

$$\Delta T_f = K_f m = 5.12\text{ }^{\circ}\text{C } m^{-1} \times 0.33\text{ } m = 1.7\text{ }^{\circ}\text{C}$$

Subtract the freezing point change observed from the pure solvent's freezing point. **Equation:**

$$\text{Freezing Temperature} = 5.5\text{ }^{\circ}\text{C} - 1.7\text{ }^{\circ}\text{C} = 3.8\text{ }^{\circ}\text{C}$$

Check Your Learning

What is the freezing point of a 1.85 *m* solution of a nonvolatile nonelectrolyte solute in nitrobenzene?

Note:

Answer:

−9.3 °C

Note:

Colligative Properties and De-Icing

Sodium chloride and its group 2 analogs calcium and magnesium chloride are often used to de-ice roadways and sidewalks, due to the fact that a solution of any one of these salts will have a freezing point lower than 0 °C, the freezing point of pure water. The group 2 metal salts are frequently mixed with the cheaper and more readily available sodium chloride (“rock salt”) for use on roads, since they tend to be somewhat less corrosive than the NaCl, and they provide a larger depression of the freezing point, since they dissociate to yield three particles per formula unit, rather than two particles like the sodium chloride.

Because these ionic compounds tend to hasten the corrosion of metal, they would not be a wise choice to use in antifreeze for the radiator in your car or to de-ice a plane prior to takeoff. For these applications, covalent compounds, such as ethylene or propylene glycol, are often used. The glycols used in radiator fluid not only lower the freezing point of the liquid, but they elevate the boiling point, making the fluid useful in both winter and summer. Heated glycols are often sprayed onto the surface of airplanes prior to takeoff in inclement weather in the winter to remove ice that has already formed and prevent the formation of more ice, which would be particularly dangerous if formed on the control surfaces of the aircraft ([link](#)).



(a)

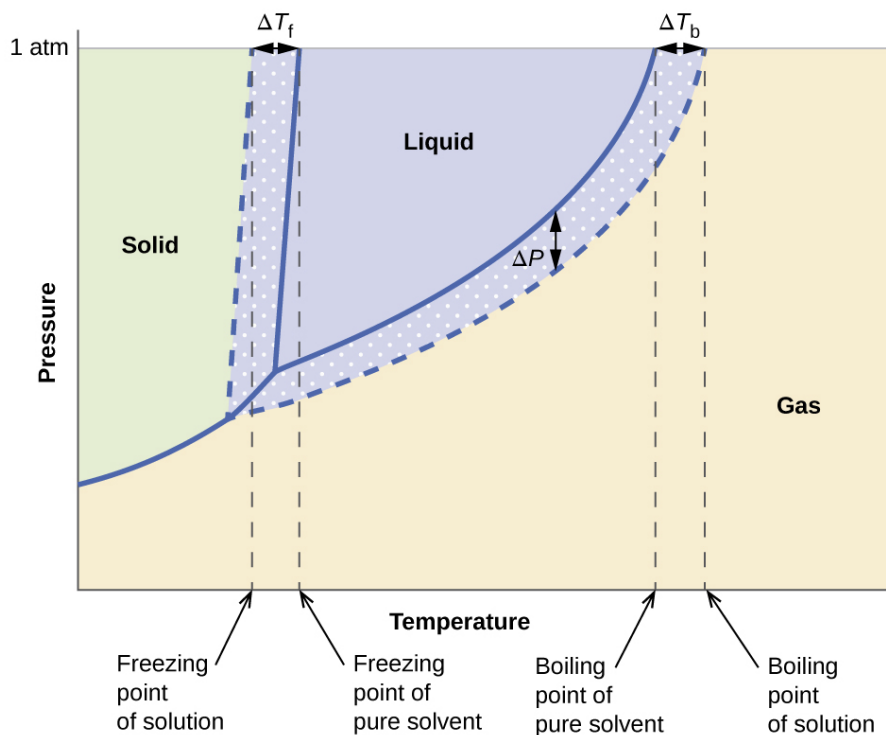


(b)

Freezing point depression is exploited to remove ice from (a) roadways and (b) the control surfaces of aircraft.

Phase Diagram for an Aqueous Solution of a Nonelectrolyte

The colligative effects on vapor pressure, boiling point, and freezing point described in the previous section are conveniently summarized by comparing the phase diagrams for a pure liquid and a solution derived from that liquid. Phase diagrams for water and an aqueous solution are shown in [\[link\]](#).



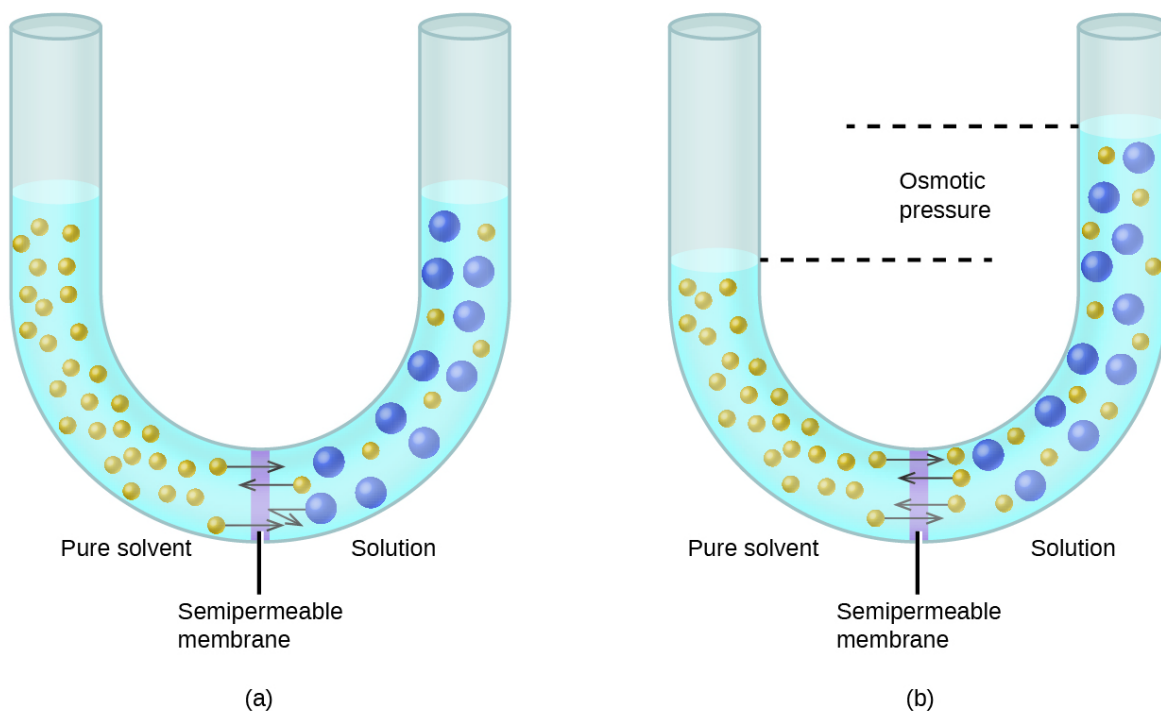
These phase diagrams show water (solid curves) and an aqueous solution of nonelectrolyte (dashed curves).

The liquid-vapor curve for the solution is located *beneath* the corresponding curve for the solvent, depicting the vapor pressure *lowering*, ΔP , that results from the dissolution of nonvolatile solute. Consequently, at any given pressure, the solution's boiling point is observed at a higher temperature than that for the pure solvent, reflecting the boiling point elevation, ΔT_b , associated with the presence of nonvolatile solute. The solid-liquid curve for the solution is displaced left of that for the pure solvent, representing the freezing point depression, ΔT_f , that accompanies solution formation. Finally, notice that the solid-gas curves for the solvent and its solution are identical. This is the case for many solutions comprising liquid solvents and nonvolatile solutes. Just as for vaporization, when a solution of this sort is frozen, it is actually just the *solvent* molecules that undergo the liquid-to-solid transition, forming pure solid solvent that excludes solute species. The solid and gaseous phases, therefore, are composed of solvent only, and so transitions between these phases are not subject to colligative effects.

Osmosis and Osmotic Pressure of Solutions

A number of natural and synthetic materials exhibit *selective permeation*, meaning that only molecules or ions of a certain size, shape, polarity, charge, and so forth, are capable of passing through (permeating) the material. Biological cell membranes provide elegant examples of selective permeation in nature, while dialysis tubing used to remove metabolic wastes from blood is a more simplistic technological example. Regardless of how they may be fabricated, these materials are generally referred to as **semipermeable membranes**.

Consider the apparatus illustrated in [\[link\]](#), in which samples of pure solvent and a solution are separated by a membrane that only solvent molecules may permeate. Solvent molecules will diffuse across the membrane in both directions. Since the concentration of *solvent* is greater in the pure solvent than the solution, these molecules will diffuse from the solvent side of the membrane to the solution side at a faster rate than they will in the reverse direction. The result is a net transfer of solvent molecules from the pure solvent to the solution. Diffusion-driven transfer of solvent molecules through a semipermeable membrane is a process known as **osmosis**.



Osmosis results in the transfer of solvent molecules from a sample of low (or zero) solute concentration to a sample of higher solute concentration.

When osmosis is carried out in an apparatus like that shown in [\[link\]](#), the volume of the solution increases as it becomes diluted by accumulation of solvent. This causes the level of the solution to rise, increasing its hydrostatic pressure (due to the weight of the column of solution in the tube) and resulting in a faster transfer of solvent molecules back to the pure solvent side. When the pressure reaches a value that yields a reverse solvent transfer rate equal to the osmosis rate, bulk transfer of solvent ceases. This pressure is called the **osmotic pressure (Π)** of the solution. The osmotic pressure of a dilute solution is related to its solute molarity, M , and absolute temperature, T , according to the equation

Equation:

$$\Pi = MRT$$

where R is the universal gas constant.

Example:

Calculation of Osmotic Pressure

What is the osmotic pressure (atm) of a 0.30 M solution of glucose in water that is used for intravenous infusion at body temperature, 37 °C?

Solution

We can find the osmotic pressure, Π , using the formula $\Pi = MRT$, where T is on the Kelvin scale (310 K) and the value of R is expressed in appropriate units (0.08206 L atm/mol K).

Equation:

$$\begin{aligned}\Pi &= MRT \\ &= 0.03 \text{ mol/L} \times 0.08206 \text{ L atm/mol K} \times 310 \text{ K} \\ &= 7.6 \text{ atm}\end{aligned}$$

Check Your Learning

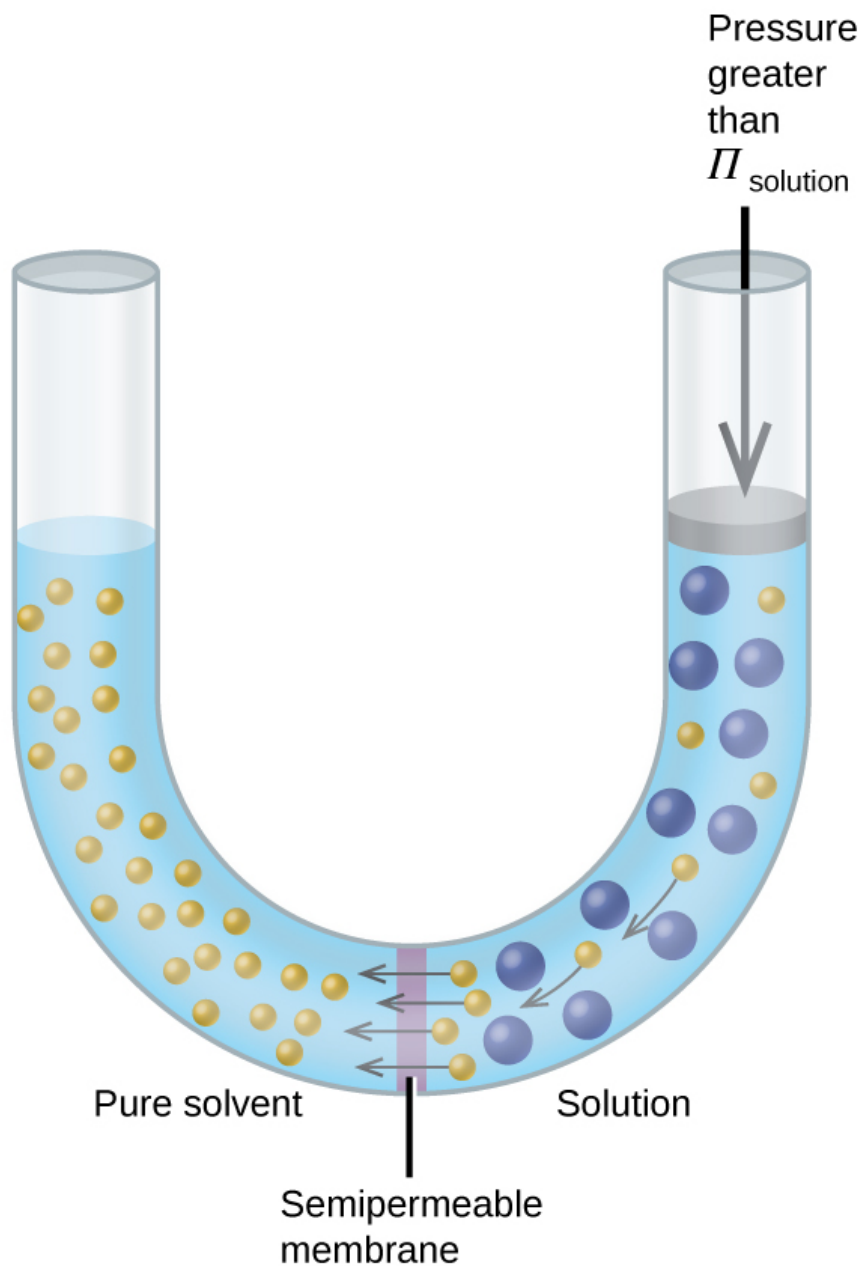
What is the osmotic pressure (atm) a solution with a volume of 0.750 L that contains 5.0 g of methanol, CH_3OH , in water at 37 °C?

Note:

Answer:

5.3 atm

If a solution is placed in an apparatus like the one shown in [\[link\]](#), applying pressure greater than the osmotic pressure of the solution reverses the osmosis and pushes solvent molecules from the solution into the pure solvent. This technique of reverse osmosis is used for large-scale desalination of seawater and on smaller scales to produce high-purity tap water for drinking.



Applying a pressure greater than the osmotic pressure of a solution will reverse osmosis. Solvent molecules from the solution are pushed into the pure solvent.

Note:

Reverse Osmosis Water Purification

In the process of osmosis, diffusion serves to move water through a semipermeable membrane from a less concentrated solution to a more concentrated solution. Osmotic pressure is the amount of

pressure that must be applied to the more concentrated solution to cause osmosis to stop. If greater pressure is applied, the water will go from the more concentrated solution to a less concentrated (more pure) solution. This is called reverse osmosis. Reverse osmosis (RO) is used to purify water in many applications, from desalination plants in coastal cities, to water-purifying machines in grocery stores ([\[link\]](#)), and smaller reverse-osmosis household units. With a hand-operated pump, small RO units can be used in third-world countries, disaster areas, and in lifeboats. Our military forces have a variety of generator-operated RO units that can be transported in vehicles to remote locations.



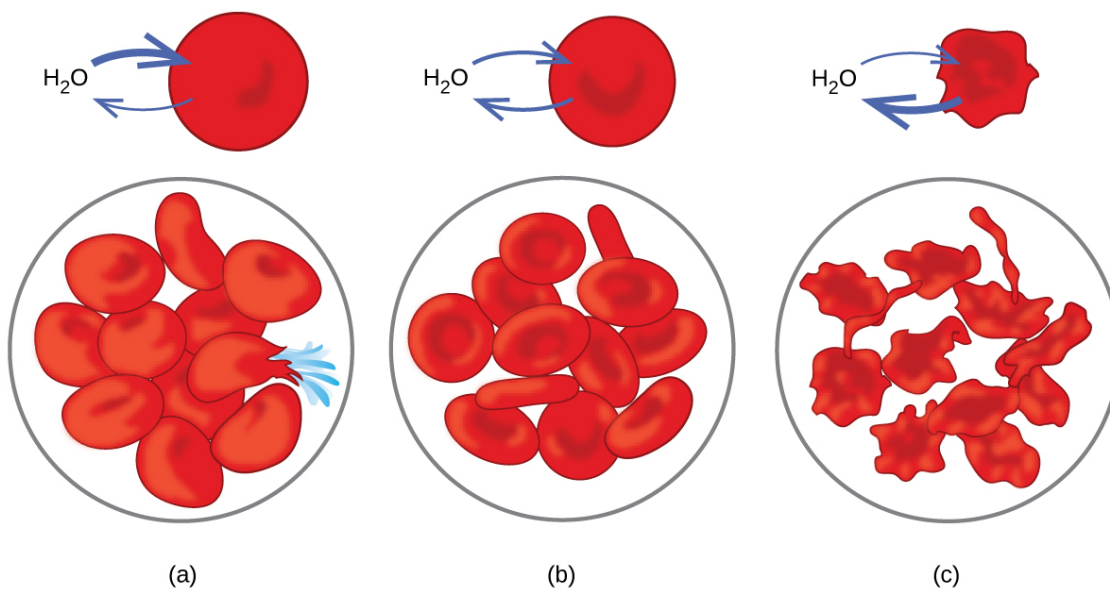
(a)



(b)

Reverse osmosis systems for purifying drinking water are shown here on (a) small and (b) large scales. (credit a: modification of work by Jerry Kirkhart; credit b: modification of work by Willard J. Lathrop)

Examples of osmosis are evident in many biological systems because cells are surrounded by semipermeable membranes. Carrots and celery that have become limp because they have lost water can be made crisp again by placing them in water. Water moves into the carrot or celery cells by osmosis. A cucumber placed in a concentrated salt solution loses water by osmosis and absorbs some salt to become a pickle. Osmosis can also affect animal cells. Solute concentrations are particularly important when solutions are injected into the body. Solute concentrations in body cell fluids and blood serum give these solutions an osmotic pressure of approximately 7.7 atm. Solutions injected into the body must have the same osmotic pressure as blood serum; that is, they should be **isotonic** with blood serum. If a less concentrated solution, a **hypotonic** solution, is injected in sufficient quantity to dilute the blood serum, water from the diluted serum passes into the blood cells by osmosis, causing the cells to expand and rupture. This process is called **hemolysis**. When a more concentrated solution, a **hypertonic** solution, is injected, the cells lose water to the more concentrated solution, shrivel, and possibly die in a process called **crenation**. These effects are illustrated in [\[link\]](#).



Red blood cell membranes are water permeable and will (a) swell and possibly rupture in a hypotonic solution; (b) maintain normal volume and shape in an isotonic solution; and (c) shrivel and possibly die in a hypertonic solution. (credit a/b/c: modifications of work by “LadyofHats”/Wikimedia commons)

Determination of Molar Masses

Osmotic pressure and changes in freezing point, boiling point, and vapor pressure are directly proportional to the concentration of solute present. Consequently, we can use a measurement of one of these properties to determine the molar mass of the solute from the measurements.

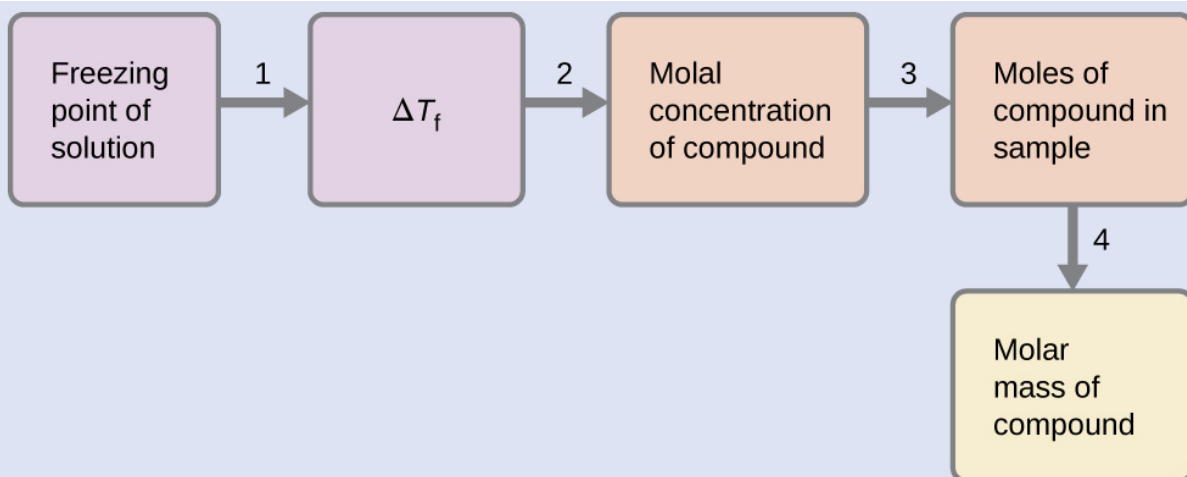
Example:

Determination of a Molar Mass from a Freezing Point Depression

A solution of 4.00 g of a nonelectrolyte dissolved in 55.0 g of benzene is found to freeze at 2.32 °C. What is the molar mass of this compound?

Solution

We can solve this problem using the following steps.



Determine the change in freezing point from the [link](#). **Equation:**
observed freezing point and the freezing point of pure benzene

$$\Delta T_f = 5.5^\circ\text{C} - 2.32^\circ\text{C} = 3.2^\circ\text{C}$$

Determine the molal concentration from K_f , the freezing point depression constant for benzene [link](#), and ΔT_f . **Equation:**

$$\Delta T_f = K_f m$$

$$m = \frac{\Delta T_f}{K_f} = \frac{3.2^\circ\text{C}}{5.12^\circ\text{C } m^{-1}} = 0.63 m$$

Determine the number of moles of compound in the solution from the molal concentration and the mass of solvent used to make the solution. **Equation:**

Moles of solute = $\frac{0.63 \text{ mol solute}}{1.00 \text{ kg solvent}} \times 0.0550 \text{ kg solvent} = 0.035 \text{ mol}$

Determine the molar mass from the mass of the solute and the number of moles in that mass. **Equation:**

$$\text{Molar mass} = \frac{4.00 \text{ g}}{0.035 \text{ mol}} = 1.1 \times 10^2 \text{ g/mol}$$

Check Your Learning

A solution of 35.7 g of a nonelectrolyte in 220.0 g of chloroform has a boiling point of 64.5°C . What is the molar mass of this compound?

Note:

Answer:

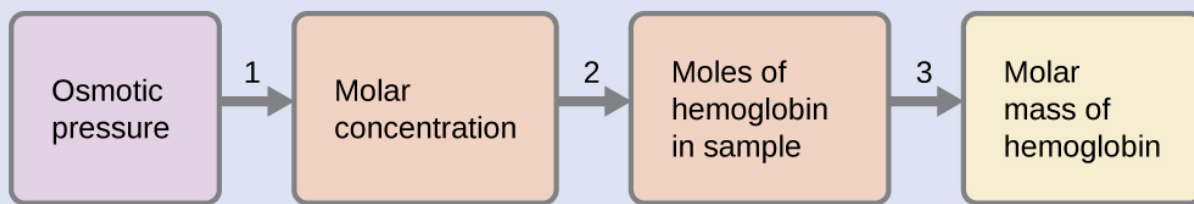
$$1.8 \times 10^2 \text{ g/mol}$$

Example:**Determination of a Molar Mass from Osmotic Pressure**

A 0.500 L sample of an aqueous solution containing 10.0 g of hemoglobin has an osmotic pressure of 5.9 torr at 22 °C. What is the molar mass of hemoglobin?

Solution

Here is one set of steps that can be used to solve the problem:



Convert the osmotic pressure to atmospheres, then determine the molar concentration from the osmotic pressure.

Equation:

$$\Pi = \frac{5.9 \text{ torr} \times 1 \text{ atm}}{760 \text{ torr}} = 7.8 \times 10^{-3} \text{ atm}$$

$$\Pi = MRT$$

$$M = \frac{\Pi}{RT} = \frac{7.8 \times 10^{-3} \text{ atm}}{(0.08206 \text{ L atm/mol K})(295 \text{ K})} = 3.2 \times 10^{-4} \text{ M}$$

Determine the number of moles of hemoglobin in the solution from the concentration and the volume of the solution.

Equation:

$$\text{moles of hemoglobin} = \frac{3.2 \times 10^{-4} \text{ mol}}{1 \text{ L solution}} \times 0.500 \text{ L solution} = 1.6 \times 10^{-4} \text{ mol}$$

Determine the molar mass from the mass of hemoglobin and the number of moles in that mass.

$$\text{molar mass} = \frac{10.0 \text{ g}}{1.6 \times 10^{-4} \text{ mol}} = 6.2 \times 10^4 \text{ g/mol}$$

Check Your Learning

What is the molar mass of a protein if a solution of 0.02 g of the protein in 25.0 mL of solution has an osmotic pressure of 0.56 torr at 25 °C?

Note:**Answer:**

$$3 \times 10^4 \text{ g/mol}$$

Colligative Properties of Electrolytes

As noted previously in this module, the colligative properties of a solution depend only on the number, not on the kind, of solute species dissolved. For example, 1 mole of any nonelectrolyte dissolved in 1 kilogram of solvent produces the same lowering of the freezing point as does 1 mole of any other nonelectrolyte. However, 1 mole of sodium chloride (an electrolyte) forms 2 moles of ions when dissolved in solution. Each individual ion produces the same effect on the freezing point as a single molecule does.

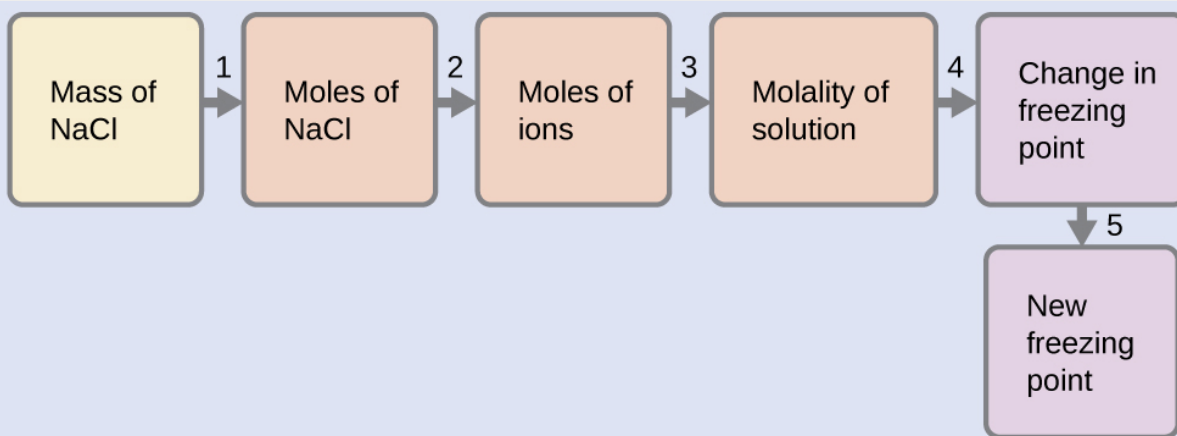
Example:

The Freezing Point of a Solution of an Electrolyte

The concentration of ions in seawater is approximately the same as that in a solution containing 4.2 g of NaCl dissolved in 125 g of water. Assume that each of the ions in the NaCl solution has the same effect on the freezing point of water as a nonelectrolyte molecule, and determine the freezing temperature the solution (which is approximately equal to the freezing temperature of seawater).

Solution

We can solve this problem using the following series of steps.



Convert from grams to moles of NaCl using the molar mass of NaCl in the unit conversion factor. Result: 0.072 mol NaCl

Determine the number of moles of ions present in the solution using the number of moles of ions in 1 mole of NaCl as the conversion factor (2 mol ions/1 mol NaCl). Result: 0.14 mol ions

Determine the molality of the ions in the solution from the number of moles of ions and the mass of solvent, in kilograms. Result: m 1.1

Use the direct proportionality between the change in freezing point and molal concentration to determine how much the freezing point changes. Result: 2.0°C

Determine the new freezing point from the freezing point of the pure solvent and the change. Result: -2.0°C Check each result as a self-assessment.

Check Your Learning

Assume that each of the ions in calcium chloride, CaCl_2 , has the same effect on the freezing point of water as a nonelectrolyte molecule. Calculate the freezing point of a solution of 0.724 g of CaCl_2 in 175 g of water.

Note:

Answer:

$-0.208\text{ }^\circ\text{C}$

Assuming complete dissociation, a 1.0 *m* aqueous solution of NaCl contains 2.0 mole of ions (1.0 mol Na^+ and 1.0 mol Cl^-) per each kilogram of water, and its freezing point depression is expected to be

Equation:

$$\Delta T_f = 2.0 \text{ mol ions/kg water} \times 1.86\text{ }^\circ\text{C kg water/mol ion} = 3.7\text{ }^\circ\text{C}.$$

When this solution is actually prepared and its freezing point depression measured, however, a value of $3.4\text{ }^\circ\text{C}$ is obtained. Similar discrepancies are observed for other ionic compounds, and the differences between the measured and expected colligative property values typically become more significant as solute concentrations increase. These observations suggest that the ions of sodium chloride (and other strong electrolytes) are not completely dissociated in solution.

To account for this and avoid the errors accompanying the assumption of total dissociation, an experimentally measured parameter named in honor of Nobel Prize-winning German chemist Jacobus Henricus van't Hoff is used. The **van't Hoff factor (*i*)** is defined as the ratio of solute particles in solution to the number of formula units dissolved:

Equation:

$$i = \frac{\text{moles of particles in solution}}{\text{moles of formula units dissolved}}$$

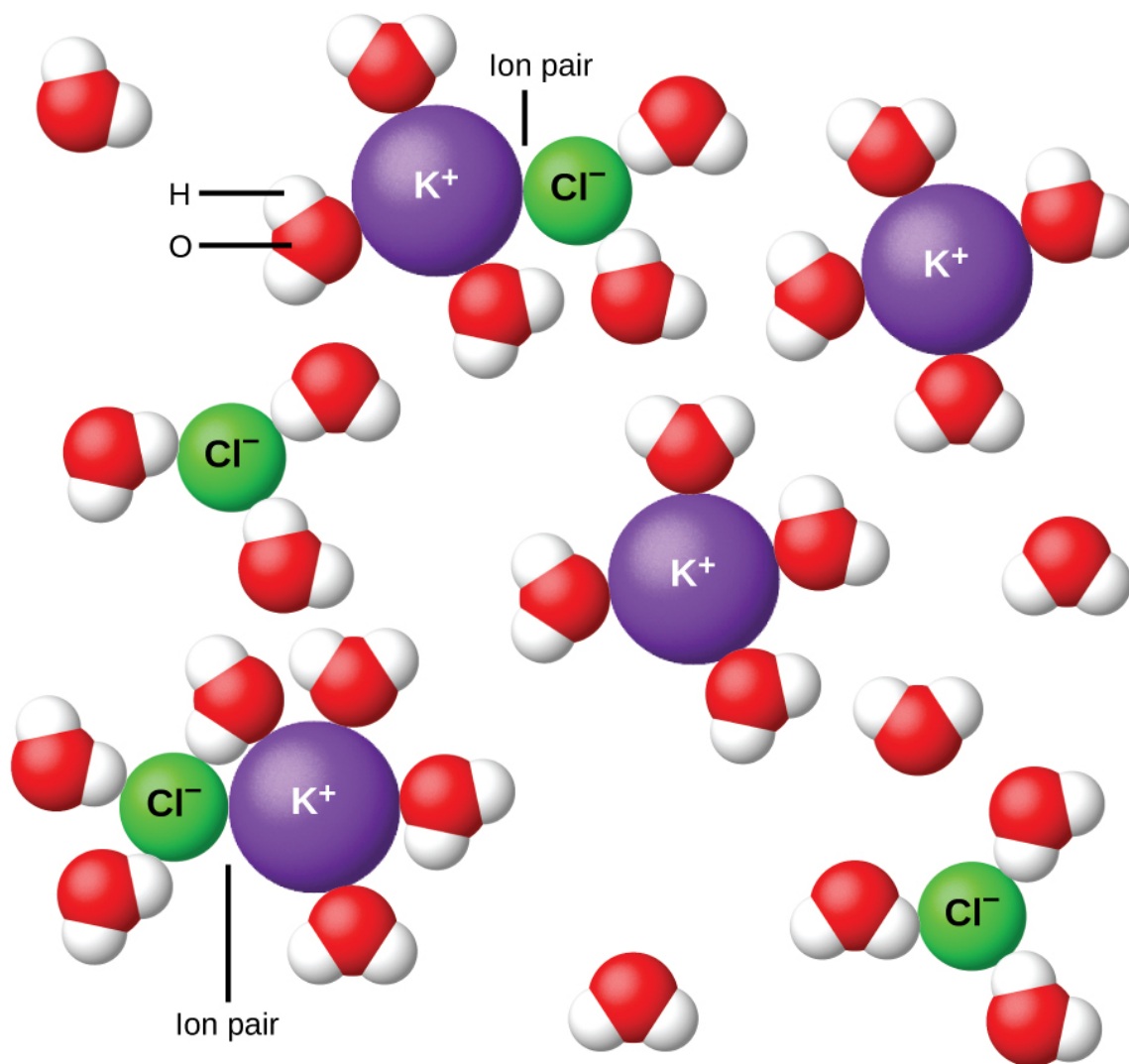
Values for measured van't Hoff factors for several solutes, along with predicted values assuming complete dissociation, are shown in [\[link\]](#).

Expected and Observed van't Hoff Factors for Several 0.050 *m* Aqueous Electrolyte Solutions

Expected and Observed van't Hoff Factor for Several 0.050 <i>m</i> Aqueous Electrolyte Solutions	Particles in Solution	<i>i</i> (Predicted)	<i>i</i> (Measured)
--	-----------------------	----------------------	---------------------

Electrolyte	Particles in Solution	<i>i</i> (Predicted)	<i>i</i> (Measured)
HCl	H ⁺ , Cl ⁻	2	1.9
NaCl	Na ⁺ , Cl ⁻	2	1.9
MgSO ₄	Mg ²⁺ , SO ₄ ²⁻	2	1.3
MgCl ₂	Mg ²⁺ , 2Cl ⁻	3	2.7
FeCl ₃	Fe ³⁺ , 3Cl ⁻	4	3.4
glucose ^[footnote] A nonelectrolyte shown for comparison.	C ₁₂ H ₂₂ O ₁₁	1	1.0

In 1923, the chemists Peter Debye and Erich Hückel proposed a theory to explain the apparent incomplete ionization of strong electrolytes. They suggested that although interionic attraction in an aqueous solution is very greatly reduced by solvation of the ions and the insulating action of the polar solvent, it is not completely nullified. The residual attractions prevent the ions from behaving as totally independent particles ([\[link\]](#)). In some cases, a positive and negative ion may actually touch, giving a solvated unit called an ion pair. Thus, the **activity**, or the effective concentration, of any particular kind of ion is less than that indicated by the actual concentration. Ions become more and more widely separated the more dilute the solution, and the residual interionic attractions become less and less. Thus, in extremely dilute solutions, the effective concentrations of the ions (their activities) are essentially equal to the actual concentrations. Note that the van't Hoff factors for the electrolytes in [\[link\]](#) are for 0.05 *m* solutions, at which concentration the value of *i* for NaCl is 1.9, as opposed to an ideal value of 2.



Ions become more and more widely separated the more dilute the solution, and the residual interionic attractions become less.

Key Concepts and Summary

Properties of a solution that depend only on the concentration of solute particles are called colligative properties. They include changes in the vapor pressure, boiling point, and freezing point of the solvent in the solution. The magnitudes of these properties depend only on the total concentration of solute particles in solution, not on the type of particles. The total concentration of solute particles in a solution also determines its osmotic pressure. This is the pressure that must be applied to the solution to prevent diffusion of molecules of pure solvent through a semipermeable membrane into the solution. Ionic compounds may not completely dissociate in solution due to activity effects, in which case observed colligative effects may be less than predicted.

Key Equations

- $(P_A = X_A P_A^\circ)$
- $P_{\text{solution}} = \sum_i P_i = \sum_i X_i P_i^\circ$
- $P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^\circ$
- $\Delta T_b = K_b m$
- $\Delta T_f = K_f m$
- $\Pi = MRT$

Chemistry End of Chapter Exercises

Exercise:

Problem:

Which is/are part of the macroscopic domain of solutions and which is/are part of the microscopic domain: boiling point elevation, Henry's law, hydrogen bond, ion-dipole attraction, molarity, nonelectrolyte, nonstoichiometric compound, osmosis, solvated ion?

Exercise:

Problem:

What is the microscopic explanation for the macroscopic behavior illustrated in [\[link\]](#)?

Solution:

The strength of the bonds between like molecules is stronger than the strength between unlike molecules. Therefore, some regions will exist in which the water molecules will exclude oil molecules and other regions will exist in which oil molecules will exclude water molecules, forming a heterogeneous region.

Exercise:

Problem:

Sketch a qualitative graph of the pressure versus time for water vapor above a sample of pure water and a sugar solution, as the liquids evaporate to half their original volume.

Exercise:

Problem:

A solution of potassium nitrate, an electrolyte, and a solution of glycerin ($\text{C}_3\text{H}_5(\text{OH})_3$), a nonelectrolyte, both boil at 100.3°C . What other physical properties of the two solutions are identical?

Solution:

Both form homogeneous solutions; their boiling point elevations are the same, as are their lowering of vapor pressures. Osmotic pressure and the lowering of the freezing point are also the same for both solutions.

Exercise:**Problem:**

What are the mole fractions of H_3PO_4 and water in a solution of 14.5 g of H_3PO_4 in 125 g of water?

- (a) Outline the steps necessary to answer the question.
- (b) Answer the question.

Exercise:**Problem:**

What are the mole fractions of HNO_3 and water in a concentrated solution of nitric acid (68.0% HNO_3 by mass)?

- (a) Outline the steps necessary to answer the question.
- (b) Answer the question.

Solution:

- (a) Find number of moles of HNO_3 and H_2O in 100 g of the solution. Find the mole fractions for the components.
- (b) The mole fraction of HNO_3 is 0.378. The mole fraction of H_2O is 0.622.

Exercise:

Problem: Calculate the mole fraction of each solute and solvent:

- (a) 583 g of H_2SO_4 in 1.50 kg of water—the acid solution used in an automobile battery
- (b) 0.86 g of NaCl in 1.00×10^2 g of water—a solution of sodium chloride for intravenous injection
- (c) 46.85 g of codeine, $\text{C}_{18}\text{H}_{21}\text{NO}_3$, in 125.5 g of ethanol, $\text{C}_2\text{H}_5\text{OH}$
- (d) 25 g of I_2 in 125 g of ethanol, $\text{C}_2\text{H}_5\text{OH}$

Exercise:

Problem: Calculate the mole fraction of each solute and solvent:

- (a) 0.710 kg of sodium carbonate (washing soda), Na_2CO_3 , in 10.0 kg of water—a saturated solution at 0°C
 - (b) 125 g of NH_4NO_3 in 275 g of water—a mixture used to make an instant ice pack
 - (c) 25 g of Cl_2 in 125 g of dichloromethane, CH_2Cl_2
 - (d) 0.372 g of tetrahydropyridine, $\text{C}_5\text{H}_9\text{N}$, in 125 g of chloroform, CHCl_3
-

Solution:

(a) $X_{\text{Na}_2\text{CO}_3} = 0.0119$; $X_{\text{H}_2\text{O}} = 0.988$; (b) $X_{\text{NH}_4\text{NO}_3} = 0.0928$; $X_{\text{H}_2\text{O}} = 0.907$; (c) $X_{\text{Cl}_2} = 0.192$; $X_{\text{CH}_2\text{Cl}_2} = 0.808$; (d) $X_{\text{C}_5\text{H}_9\text{N}} = 0.00426$; $X_{\text{CHCl}_3} = 0.997$

Exercise:**Problem:**

Calculate the mole fractions of methanol, CH_3OH ; ethanol, $\text{C}_2\text{H}_5\text{OH}$; and water in a solution that is 40% methanol, 40% ethanol, and 20% water by mass. (Assume the data are good to two significant figures.)

Exercise:

Problem: What is the difference between a 1 *M* solution and a 1 *m* solution?

Solution:

In a 1 *M* solution, the mole is contained in exactly 1 L of solution. In a 1 *m* solution, the mole is contained in exactly 1 kg of solvent.

Exercise:**Problem:**

What is the molality of phosphoric acid, H_3PO_4 , in a solution of 14.5 g of H_3PO_4 in 125 g of water?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

Exercise:**Problem:**

What is the molality of nitric acid in a concentrated solution of nitric acid (68.0% HNO_3 by mass)?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

Solution:

(a) Determine the molar mass of HNO_3 . Determine the number of moles of acid in the solution. From the number of moles and the mass of solvent, determine the molality. (b) 33.7 *m*

Exercise:

Problem: Calculate the molality of each of the following solutions:

(a) 583 g of H_2SO_4 in 1.50 kg of water—the acid solution used in an automobile battery

(b) 0.86 g of NaCl in 1.00×10^2 g of water—a solution of sodium chloride for intravenous injection

(c) 46.85 g of codeine, $\text{C}_{18}\text{H}_{21}\text{NO}_3$, in 125.5 g of ethanol, $\text{C}_2\text{H}_5\text{OH}$

(d) 25 g of I_2 in 125 g of ethanol, $\text{C}_2\text{H}_5\text{OH}$

Exercise:

Problem: Calculate the molality of each of the following solutions:

(a) 0.710 kg of sodium carbonate (washing soda), Na_2CO_3 , in 10.0 kg of water—a saturated solution at 0°C

(b) 125 g of NH_4NO_3 in 275 g of water—a mixture used to make an instant ice pack

(c) 25 g of Cl_2 in 125 g of dichloromethane, CH_2Cl_2

(d) 0.372 g of tetrahydropyridine, $\text{C}_5\text{H}_9\text{N}$, in 125 g of chloroform, CHCl_3

Solution:

(a) $6.70 \times 10^{-1} m$; (b) $5.67 m$; (c) $2.8 m$; (d) $0.0358 m$

Exercise:

Problem:

The concentration of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, in normal spinal fluid is $\frac{75 \text{ mg}}{100 \text{ g}}$. What is the molality of the solution?

Exercise:

Problem:

A 13.0% solution of K_2CO_3 by mass has a density of 1.09 g/cm^3 . Calculate the molality of the solution.

Solution:

$1.08 m$

Exercise:

Problem:

Why does 1 mol of sodium chloride depress the freezing point of 1 kg of water almost twice as much as 1 mol of glycerin?

Exercise:

Problem:

What is the boiling point of a solution of 115.0 g of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, in 350.0 g of water?

(a) Outline the steps necessary to answer the question

(b) Answer the question

Solution:

(a) Determine the molar mass of sucrose; determine the number of moles of sucrose in the solution; convert the mass of solvent to units of kilograms; from the number of moles and the mass of solvent, determine the molality; determine the difference between the boiling point of water and the boiling point of the solution; determine the new boiling point. (b) 100.5 °C

Exercise:

Problem:

What is the boiling point of a solution of 9.04 g of I₂ in 75.5 g of benzene, assuming the I₂ is nonvolatile?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

Exercise:

Problem:

What is the freezing temperature of a solution of 115.0 g of sucrose, C₁₂H₂₂O₁₁, in 350.0 g of water, which freezes at 0.0 °C when pure?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

Solution:

(a) Determine the molar mass of sucrose; determine the number of moles of sucrose in the solution; convert the mass of solvent to units of kilograms; from the number of moles and the mass of solvent, determine the molality; determine the difference between the freezing temperature of water and the freezing temperature of the solution; determine the new freezing temperature. (b) -1.8 °C

Exercise:

Problem: What is the freezing point of a solution of 9.04 g of I₂ in 75.5 g of benzene?

(a) Outline the steps necessary to answer the following question.

(b) Answer the question.

Exercise:

Problem:

What is the osmotic pressure of an aqueous solution of 1.64 g of Ca(NO₃)₂ in water at 25 °C? The volume of the solution is 275 mL.

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

Solution:

(a) Determine the molar mass of $\text{Ca}(\text{NO}_3)_2$; determine the number of moles of $\text{Ca}(\text{NO}_3)_2$ in the solution; determine the number of moles of ions in the solution; determine the molarity of ions, then the osmotic pressure. (b) 2.67 atm

Exercise:

Problem:

What is osmotic pressure of a solution of bovine insulin (molar mass, 5700 g mol^{-1}) at 18°C if 100.0 mL of the solution contains 0.103 g of the insulin?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

Exercise:

Problem:

What is the molar mass of a solution of 5.00 g of a compound in 25.00 g of carbon tetrachloride (bp 76.8°C ; $K_b = 5.02^\circ\text{C}/m$) that boils at 81.5°C at 1 atm?

(a) Outline the steps necessary to answer the question.

(b) Solve the problem.

Solution:

(a) Determine the molal concentration from the change in boiling point and K_b ; determine the moles of solute in the solution from the molal concentration and mass of solvent; determine the molar mass from the number of moles and the mass of solute. (b) $2.1 \times 10^2 \text{ g mol}^{-1}$

Exercise:

Problem:

A sample of an organic compound (a nonelectrolyte) weighing 1.35 g lowered the freezing point of 10.0 g of benzene by 3.66°C . Calculate the molar mass of the compound.

Exercise:

Problem:

A 1.0 *m* solution of HCl in benzene has a freezing point of 0.4°C . Is HCl an electrolyte in benzene? Explain.

Solution:

No. Pure benzene freezes at 5.5°C , and so the observed freezing point of this solution is depressed by $\Delta T_f = 5.5 - 0.4 = 5.1^\circ\text{C}$. The value computed, assuming no ionization of HCl, is

$\Delta T_f = (1.0\text{ m})(5.14\text{ }^\circ\text{C}/m) = 5.1\text{ }^\circ\text{C}$. Agreement of these values supports the assumption that HCl is not ionized.

Exercise:

Problem:

A solution contains 5.00 g of urea, $\text{CO}(\text{NH}_2)_2$, a nonvolatile compound, dissolved in 0.100 kg of water. If the vapor pressure of pure water at $25\text{ }^\circ\text{C}$ is 23.7 torr, what is the vapor pressure of the solution?

Exercise:

Problem:

A 12.0-g sample of a nonelectrolyte is dissolved in 80.0 g of water. The solution freezes at $-1.94\text{ }^\circ\text{C}$. Calculate the molar mass of the substance.

Solution:

144 g mol^{-1}

Exercise:

Problem:

Arrange the following solutions in order by their decreasing freezing points: $0.1\text{ m Na}_3\text{PO}_4$, $0.1\text{ m C}_2\text{H}_5\text{OH}$, 0.01 m CO_2 , 0.15 m NaCl , and 0.2 m CaCl_2 .

Exercise:

Problem:

Calculate the boiling point elevation of 0.100 kg of water containing 0.010 mol of NaCl, 0.020 mol of Na_2SO_4 , and 0.030 mol of MgCl_2 , assuming complete dissociation of these electrolytes.

Solution:

$0.870\text{ }^\circ\text{C}$

Exercise:

Problem:

How could you prepare a 3.08 m aqueous solution of glycerin, $\text{C}_3\text{H}_8\text{O}_3$? What is the freezing point of this solution?

Exercise:

Problem:

A sample of sulfur weighing 0.210 g was dissolved in 17.8 g of carbon disulfide, CS_2 ($K_b = 2.43\text{ }^\circ\text{C}/m$). If the boiling point elevation was $0.107\text{ }^\circ\text{C}$, what is the formula of a sulfur molecule in carbon disulfide?

Solution:

S₈

Exercise:

Problem:

In a significant experiment performed many years ago, 5.6977 g of cadmium iodide in 44.69 g of water raised the boiling point 0.181 °C. What does this suggest about the nature of a solution of CdI₂?

Exercise:

Problem:

Lysozyme is an enzyme that cleaves cell walls. A 0.100-L sample of a solution of lysozyme that contains 0.0750 g of the enzyme exhibits an osmotic pressure of 1.32×10^{-3} atm at 25 °C. What is the molar mass of lysozyme?

Solution:

$$1.39 \times 10^4 \text{ g mol}^{-1}$$

Exercise:

Problem:

The osmotic pressure of a solution containing 7.0 g of insulin per liter is 23 torr at 25 °C. What is the molar mass of insulin?

Exercise:

Problem:

The osmotic pressure of human blood is 7.6 atm at 37 °C. What mass of glucose, C₆H₁₂O₆, is required to make 1.00 L of aqueous solution for intravenous feeding if the solution must have the same osmotic pressure as blood at body temperature, 37 °C?

Solution:

54 g

Exercise:

Problem:

What is the freezing point of a solution of dibromobenzene, C₆H₄Br₂, in 0.250 kg of benzene, if the solution boils at 83.5 °C?

Exercise:

Problem:

What is the boiling point of a solution of NaCl in water if the solution freezes at −0.93 °C?

Solution:

100.26 °C

Exercise:**Problem:**

The sugar fructose contains 40.0% C, 6.7% H, and 53.3% O by mass. A solution of 11.7 g of fructose in 325 g of ethanol has a boiling point of 78.59 °C. The boiling point of ethanol is 78.35 °C, and K_b for ethanol is 1.20 °C/m. What is the molecular formula of fructose?

Exercise:**Problem:**

The vapor pressure of methanol, CH₃OH, is 94 torr at 20 °C. The vapor pressure of ethanol, C₂H₅OH, is 44 torr at the same temperature.

- (a) Calculate the mole fraction of methanol and of ethanol in a solution of 50.0 g of methanol and 50.0 g of ethanol.
- (b) Ethanol and methanol form a solution that behaves like an ideal solution. Calculate the vapor pressure of methanol and of ethanol above the solution at 20 °C.
- (c) Calculate the mole fraction of methanol and of ethanol in the vapor above the solution.

Solution:

(a) $X_{\text{CH}_3\text{OH}} = 0.590$; $X_{\text{C}_2\text{H}_5\text{OH}} = 0.410$; (b) Vapor pressures are: CH₃OH: 55 torr; C₂H₅OH: 18 torr; (c) CH₃OH: 0.75; C₂H₅OH: 0.25

Exercise:**Problem:**

The triple point of air-free water is defined as 273.16 K. Why is it important that the water be free of air?

Exercise:**Problem:**

Meat can be classified as fresh (not frozen) even though it is stored at -1 °C. Why wouldn't meat freeze at this temperature?

Solution:

The ions and compounds present in the water in the beef lower the freezing point of the beef below -1 °C.

Exercise:**Problem:**

An organic compound has a composition of 93.46% C and 6.54% H by mass. A solution of 0.090 g of this compound in 1.10 g of camphor melts at 158.4 °C. The melting point of pure camphor is 178.4 °C. K_f for camphor is 37.7 °C/m. What is the molecular formula of the solute? Show your calculations.

Exercise:**Problem:**

A sample of HgCl_2 weighing 9.41 g is dissolved in 32.75 g of ethanol, $\text{C}_2\text{H}_5\text{OH}$ ($K_b = 1.20\text{ }^\circ\text{C}/m$). The boiling point elevation of the solution is $1.27\text{ }^\circ\text{C}$. Is HgCl_2 an electrolyte in ethanol? Show your calculations.

Solution:

$$\Delta b_p = K_b m = (1.20\text{ }^\circ\text{C}/m) \left(\frac{9.41\text{ g} \times \frac{1\text{ mol HgCl}_2}{271.496\text{ g}}}{0.03275\text{ kg}} \right) = 1.27\text{ }^\circ\text{C}$$

The observed change equals the theoretical change; therefore, no dissociation occurs.

Exercise:**Problem:**

A salt is known to be an alkali metal fluoride. A quick approximate determination of freezing point indicates that 4 g of the salt dissolved in 100 g of water produces a solution that freezes at about $-1.4\text{ }^\circ\text{C}$. What is the formula of the salt? Show your calculations.

Glossary

boiling point elevation

elevation of the boiling point of a liquid by addition of a solute

boiling point elevation constant

the proportionality constant in the equation relating boiling point elevation to solute molality; also known as the ebullioscopic constant

colligative property

property of a solution that depends only on the concentration of a solute species

crenation

process whereby biological cells become shriveled due to loss of water by osmosis

freezing point depression

lowering of the freezing point of a liquid by addition of a solute

freezing point depression constant

(also, cryoscopic constant) proportionality constant in the equation relating freezing point depression to solute molality

hemolysis

rupture of red blood cells due to the accumulation of excess water by osmosis

hypertonic

of greater osmotic pressure

hypotonic

of less osmotic pressure

ion pair

solvated anion/cation pair held together by moderate electrostatic attraction

isotonic

of equal osmotic pressure

molality (m)

a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms

osmosis

diffusion of solvent molecules through a semipermeable membrane

osmotic pressure (Π)

opposing pressure required to prevent bulk transfer of solvent molecules through a semipermeable membrane

Raoult's law

the partial pressure exerted by a solution component is equal to the product of the component's mole fraction in the solution and its equilibrium vapor pressure in the pure state

semipermeable membrane

a membrane that selectively permits passage of certain ions or molecules

van't Hoff factor (i)

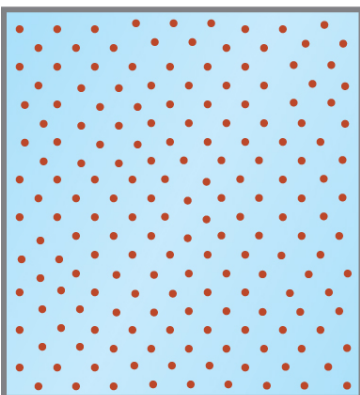
the ratio of the number of moles of particles in a solution to the number of moles of formula units dissolved in the solution

Colloids

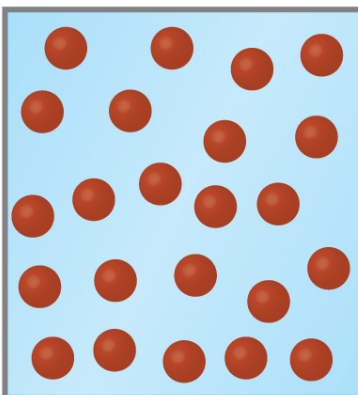
By the end of this section, you will be able to:

- Describe the composition and properties of colloidal dispersions
- List and explain several technological applications of colloids

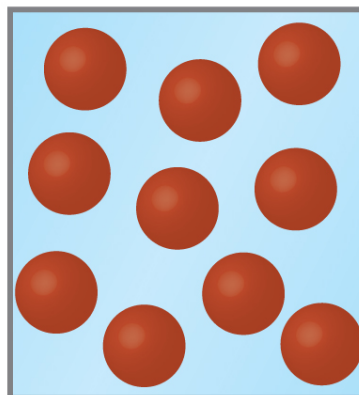
As a child, you may have made suspensions such as mixtures of mud and water, flour and water, or a suspension of solid pigments in water, known as tempera paint. These suspensions are heterogeneous mixtures composed of relatively large particles that are visible (or that can be seen with a magnifying glass). They are cloudy, and the suspended particles settle out after mixing. On the other hand, when we make a solution, we prepare a homogeneous mixture in which no settling occurs and in which the dissolved species are molecules or ions. Solutions exhibit completely different behavior from suspensions. A solution may be colored, but it is transparent, the molecules or ions are invisible, and they do not settle out on standing. A group of mixtures called **colloids** (or **colloidal dispersions**) exhibit properties intermediate between those of suspensions and solutions ([\[link\]](#)). The particles in a colloid are larger than most simple molecules; however, colloidal particles are small enough that they do not settle out upon standing.



(a)



(b)



(c)

(a) A solution is a homogeneous mixture that appears clear, such as the saltwater in this aquarium. (b) In a colloid, such as milk, the particles are

much larger but remain dispersed and do not settle. (c) A suspension, such as mud, is a heterogeneous mixture of suspended particles that appears cloudy and in which the particles can settle. (credit a photo: modification of work by Adam Wimsatt; credit b photo: modification of work by Melissa Wiese; credit c photo: modification of work by Peter Burgess)

The particles in a colloid are large enough to scatter light, a phenomenon called the **Tyndall effect**. This can make colloidal mixtures appear cloudy or opaque, such as the searchlight beams shown in [\[link\]](#). Clouds are colloidal mixtures. They are composed of water droplets that are much larger than molecules, but that are small enough that they do not settle out.



The paths of searchlight beams are made visible when light is scattered by colloidal-size particles in the air (fog, smoke, etc.). (credit: “Bahman”/Wikimedia Commons)

The term “colloid”—from the Greek words *kolla*, meaning “glue,” and *eidos*, meaning “like”—was first used in 1861 by Thomas Graham to classify mixtures such as starch in water and gelatin. Many colloidal particles are aggregates of hundreds or thousands of molecules, but others (such as proteins and polymer molecules) consist of a single extremely large molecule. The protein and synthetic polymer molecules that form colloids may have molecular masses ranging from a few thousand to many million atomic mass units.

Analogous to the identification of solution components as “solute” and “solvent,” the components of a colloid are likewise classified according to their relative amounts. The particulate component typically present in a relatively minor amount is called the **dispersed phase** and the substance or solution throughout which the particulate is dispersed is called the **dispersion medium**. Colloids may involve virtually any combination of physical states (gas in liquid, liquid in solid, solid in gas, etc.), as illustrated by the examples of colloidal systems given in [\[link\]](#).

Examples of Colloidal Systems			
Dispersed Phase	Dispersion Medium	Common Examples	Name
solid	gas	smoke, dust	—
solid	liquid	starch in water, some inks, paints, milk of magnesia	sol
solid	solid	some colored gems, some alloys	—
liquid	gas	clouds, fogs, mists, sprays	aerosol
liquid	liquid	milk, mayonnaise, butter	emulsion

Examples of Colloidal Systems			
Dispersed Phase	Dispersion Medium	Common Examples	Name
liquid	solid	jellies, gels, pearl, opal (H ₂ O in SiO ₂)	gel
gas	liquid	foams, whipped cream, beaten egg whites	foam
gas	solid	pumice, floating soaps	—

Preparation of Colloidal Systems

We can prepare a colloidal system by producing particles of colloidal dimensions and distributing these particles throughout a dispersion medium. Particles of colloidal size are formed by two methods:

1. Dispersion methods: that is, by breaking down larger particles. For example, paint pigments are produced by dispersing large particles by grinding in special mills.
2. Condensation methods: that is, growth from smaller units, such as molecules or ions. For example, clouds form when water molecules condense and form very small droplets.

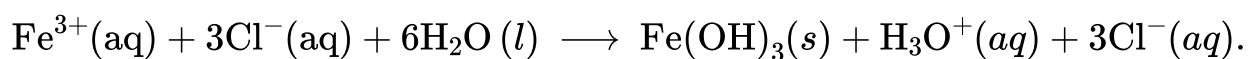
A few solid substances, when brought into contact with water, disperse spontaneously and form colloidal systems. Gelatin, glue, starch, and dehydrated milk powder behave in this manner. The particles are already of colloidal size; the water simply disperses them. Powdered milk particles of colloidal size are produced by dehydrating milk spray. Some atomizers produce colloidal dispersions of a liquid in air.

We can prepare an **emulsion** by shaking together or blending two immiscible liquids. This breaks one liquid into droplets of colloidal size, which then disperse throughout the other liquid. Oil spills in the ocean may be difficult to clean up, partly because wave action can cause the oil and water to form an emulsion. In many emulsions, however, the dispersed phase tends to coalesce, form large drops, and separate. Therefore, emulsions are usually stabilized by an

emulsifying agent, a substance that inhibits the coalescence of the dispersed liquid. For example, a little soap will stabilize an emulsion of kerosene in water. Milk is an emulsion of butterfat in water, with the protein casein as the emulsifying agent. Mayonnaise is an emulsion of oil in vinegar, with egg yolk components as the emulsifying agents.

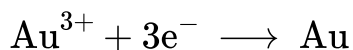
Condensation methods form colloidal particles by aggregation of molecules or ions. If the particles grow beyond the colloidal size range, drops or precipitates form, and no colloidal system results. Clouds form when water molecules aggregate and form colloid-sized particles. If these water particles coalesce to form adequately large water drops of liquid water or crystals of solid water, they settle from the sky as rain, sleet, or snow. Many condensation methods involve chemical reactions. We can prepare a red colloidal suspension of iron(III) hydroxide by mixing a concentrated solution of iron(III) chloride with hot water:

Equation:



A colloidal gold sol results from the reduction of a very dilute solution of gold(III) chloride by a reducing agent such as formaldehyde, tin(II) chloride, or iron(II) sulfate:

Equation:

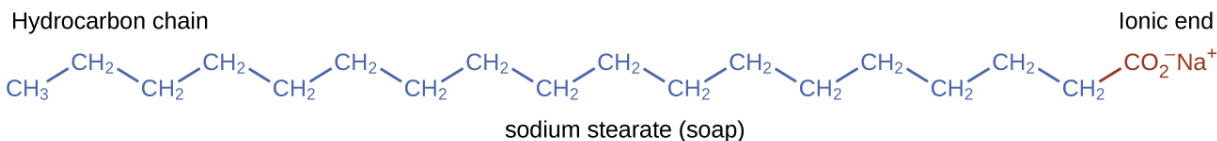


Some gold sols prepared in 1857 are still intact (the particles have not coalesced and settled), illustrating the long-term stability of many colloids.

Soaps and Detergents

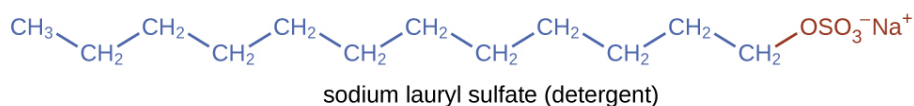
Pioneers made soap by boiling fats with a strongly basic solution made by leaching potassium carbonate, K_2CO_3 , from wood ashes with hot water. Animal fats contain polyesters of fatty acids (long-chain carboxylic acids). When animal fats are treated with a base like potassium carbonate or sodium hydroxide, glycerol and salts of fatty acids such as palmitic, oleic, and stearic acid are formed. The salts of fatty acids are called *soaps*. The sodium salt of stearic acid, sodium stearate, has the formula $\text{C}_{17}\text{H}_{35}\text{CO}_2\text{Na}$ and contains an uncharged

nonpolar hydrocarbon chain, the $\text{C}_{17}\text{H}_{35}$ — unit, and an ionic carboxylate group, the —CO_2^- unit ([\[link\]](#)).



Soaps contain a nonpolar hydrocarbon end (blue) and an ionic end (red). The ionic end is a carboxylate group. The length of the hydrocarbon end can vary from soap to soap.

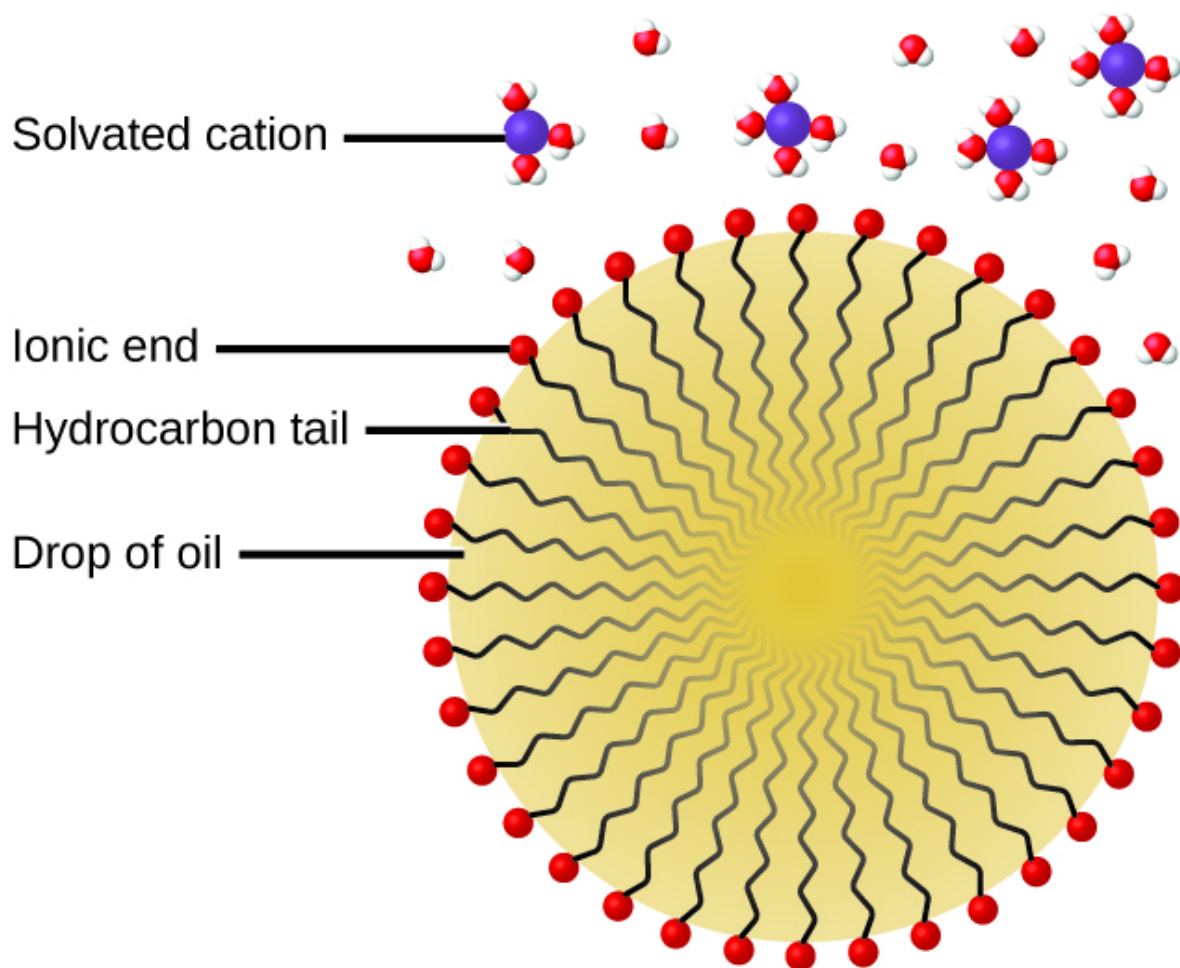
Detergents (soap substitutes) also contain nonpolar hydrocarbon chains, such as $\text{C}_{12}\text{H}_{25}$ —, and an ionic group, such as a sulfate— OSO_3^- , or a sulfonate— SO_3^- ([\[link\]](#)). Soaps form insoluble calcium and magnesium compounds in hard water; detergents form water-soluble products—a definite advantage for detergents.



Detergents contain a nonpolar hydrocarbon end (blue) and an ionic end (red). The ionic end can be either a sulfate or a sulfonate. The length of the hydrocarbon end can vary from detergent to detergent.

The cleaning action of soaps and detergents can be explained in terms of the structures of the molecules involved. The hydrocarbon (nonpolar) end of a soap or detergent molecule dissolves in, or is attracted to, nonpolar substances such as oil, grease, or dirt particles. The ionic end is attracted by water (polar), illustrated in [\[link\]](#). As a result, the soap or detergent molecules become oriented at the interface between the dirt particles and the water so they act as a kind of bridge between two different kinds of matter, nonpolar and polar. Molecules such as this are termed **amphiphilic** since they have both a hydrophobic (“water-fearing”)

part and a hydrophilic (“water-loving”) part. As a consequence, dirt particles become suspended as colloidal particles and are readily washed away.



This diagrammatic cross section of an emulsified drop of oil in water shows how soap or detergent acts as an emulsifier.

Note:

Deepwater Horizon Oil Spill

The blowout of the Deepwater Horizon oil drilling rig on April 20, 2010, in the Gulf of Mexico near Mississippi began the largest marine oil spill in the history

of the petroleum industry. In the 87 days following the blowout, an estimated 4.9 million barrels (210 million gallons) of oil flowed from the ruptured well 5000 feet below the water's surface. The well was finally declared sealed on September 19, 2010.

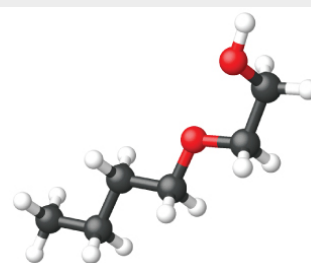
Crude oil is immiscible with and less dense than water, so the spilled oil rose to the surface of the water. Floating booms, skimmer ships, and controlled burns were used to remove oil from the water's surface in an attempt to protect beaches and wetlands along the Gulf coast. In addition to removal of the oil, attempts were also made to lessen its environmental impact by rendering it "soluble" (in the loose sense of the term) and thus allowing it to be diluted to hopefully less harmful levels by the vast volume of ocean water. This approach used 1.84 million gallons of the oil dispersant Corexit 9527, most of which was injected underwater at the site of the leak, with small amounts being sprayed on top of the spill. Corexit 9527 contains 2-butoxyethanol ($C_6H_{14}O_2$), an amphiphilic molecule whose polar and nonpolar ends are useful for emulsifying oil into small droplets, increasing the surface area of the oil and making it more available to marine bacteria for digestion ([\[link\]](#)). While this approach avoids many of the immediate hazards that bulk oil poses to marine and coastal ecosystems, it introduces the possibility of long-term effects resulting from the introduction of the complex and potential toxic components of petroleum into the ocean's food chain. A number of organizations are involved in monitoring the extended impact of this oil spill, including the National Oceanic and Atmospheric Administration (visit this [website](#) for additional details).



(a)



(b)



(c)

(a) This NASA satellite image shows the oil slick from the Deepwater Horizon spill. (b) A US Air Force plane sprays Corexit, a dispersant. (c)

The molecular structure of 2-butoxyethanol is shown. (credit a: modification of work by "NASA, FT2, demis.nl"/Wikimedia Commons; credit b: modification of work by "NASA/MODIS Rapid Response Team"/Wikimedia Commons)

Electrical Properties of Colloidal Particles

Dispersed colloidal particles are often electrically charged. A colloidal particle of iron(III) hydroxide, for example, does not contain enough hydroxide ions to compensate exactly for the positive charges on the iron(III) ions. Thus, each individual colloidal particle bears a positive charge, and the colloidal dispersion consists of charged colloidal particles and some free hydroxide ions, which keep the dispersion electrically neutral. Most metal hydroxide colloids have positive charges, whereas most metals and metal sulfides form negatively charged dispersions. All colloidal particles in any one system have charges of the same sign. This helps keep them dispersed because particles containing like charges repel each other.

We can take advantage of the charge on colloidal particles to remove them from a variety of mixtures. If we place a colloidal dispersion in a container with charged electrodes, positively charged particles, such as iron(III) hydroxide particles, would move to the negative electrode. There, the colloidal particles lose their charge and coagulate as a precipitate.

The carbon and dust particles in smoke are often colloiddally dispersed and electrically charged. Frederick Cottrell, an American chemist, developed a process to remove these particles.

Note:

Frederick Gardner Cottrell



(a)

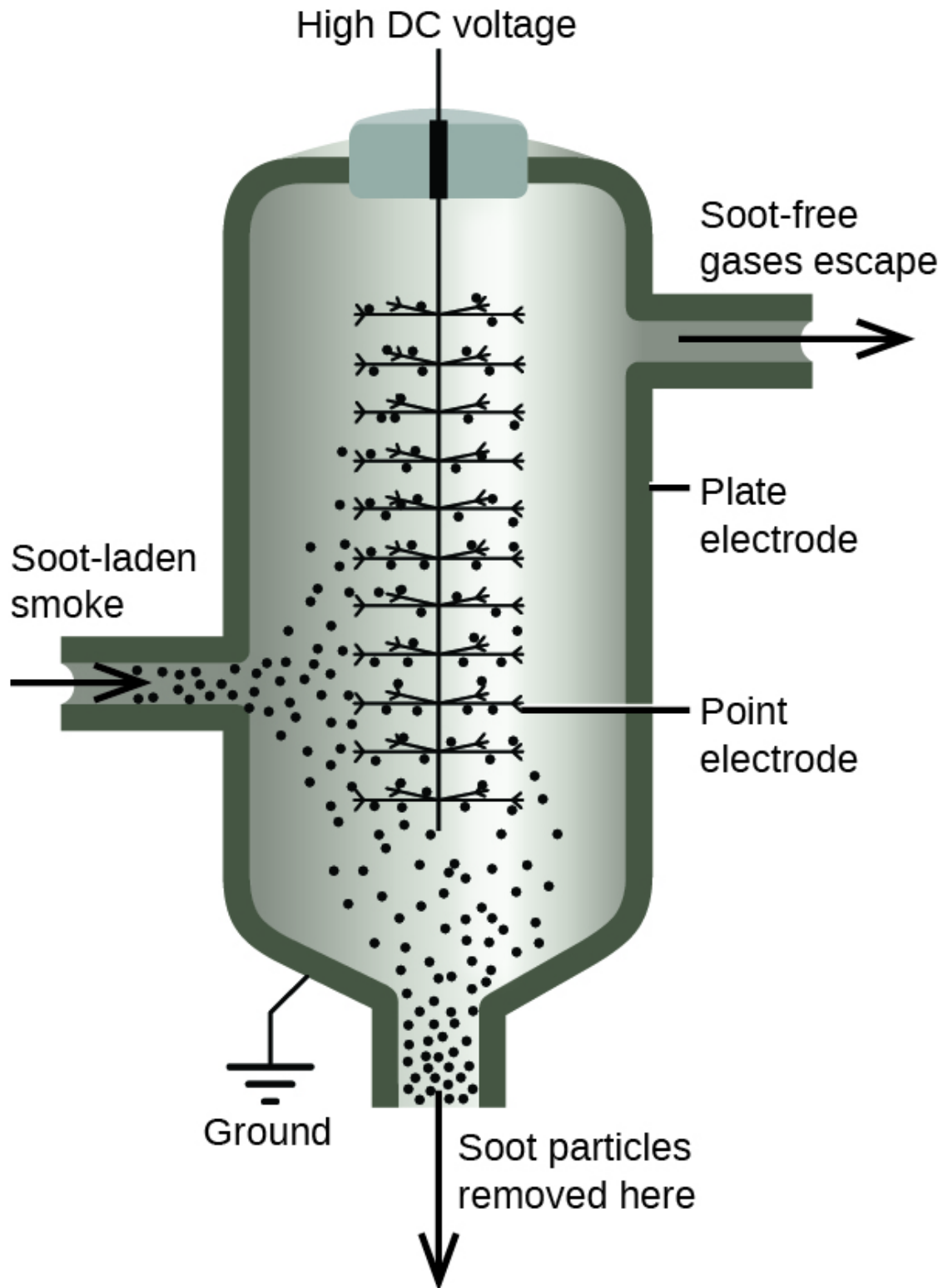


(b)

(a) Frederick Cottrell developed (b) the electrostatic precipitator, a device designed to curb air pollution by removing colloidal particles from air. (credit b: modification of work by “SpLot”/Wikimedia Commons)

Born in Oakland, CA in 1877, Frederick Cottrell devoured textbooks as if they were novels and graduated from high school at the age of 16. He then entered the University of California (UC), Berkeley, completing a Bachelor's degree in three years. He saved money from his \$1200 annual salary as a chemistry teacher at Oakland High School to fund his studies in chemistry in Berlin with Nobel prize winner Jacobus Henricus van't Hoff, and in Leipzig with Wilhelm Ostwald, another Nobel awardee. After earning his PhD in physical chemistry, he returned to the United States to teach at UC Berkeley. He also consulted for the DuPont Company, where he developed the electrostatic precipitator, a device designed to curb air pollution by removing colloidal particles from air. Cottrell used the proceeds from his invention to fund a nonprofit research corporation to finance scientific research.

The charged particles are attracted to highly charged electrodes, where they are neutralized and deposited as dust ([link](#)). This is one of the important methods used to clean up the smoke from a variety of industrial processes. The process is also important in the recovery of valuable products from the smoke and flue dust of smelters, furnaces, and kilns. There are also ionic air filters designed for home use to improve indoor air quality.

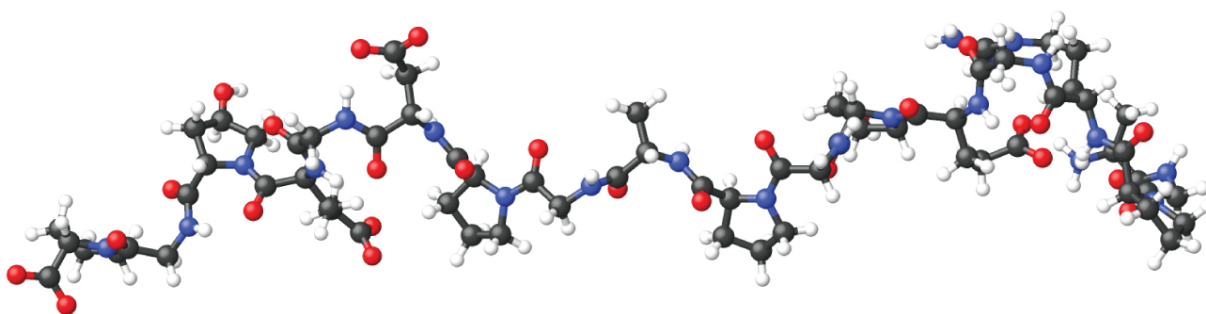


In a Cottrell precipitator, positively and negatively charged particles are attracted to highly charged electrodes, where they are neutralized and

deposited as dust.

Gels

When we make gelatin, such as Jell-O, we are making a type of colloid ([\[link\]](#)). Gelatin sets on cooling because the hot aqueous mixture of gelatin coagulates as it cools and the whole mass, including the liquid, sets to an extremely viscous body known as a **gel**, a colloid in which the dispersing medium is a solid and the dispersed phase is a liquid. It appears that the fibers of the dispersing medium form a complex three-dimensional network, the interstices being filled with the liquid medium or a dilute solution of the dispersing medium. Because the formation of a gel is accompanied by the taking up of water or some other solvent, the gel is said to be hydrated or solvated.



Gelatin desserts are colloids in which an aqueous solution of sweeteners and flavors is dispersed throughout a medium of solid proteins. (credit photo: modification of work by Steven Depolo)

Pectin, a carbohydrate from fruit juices, is a gel-forming substance important in jelly making. Silica gel, a colloidal dispersion of hydrated silicon dioxide, is formed when dilute hydrochloric acid is added to a dilute solution of sodium silicate. Canned Heat is a gel made by mixing alcohol and a saturated aqueous solution of calcium acetate.

Key Concepts and Summary

Colloids are mixtures in which one or more substances are dispersed as relatively large solid particles or liquid droplets throughout a solid, liquid, or gaseous medium. The particles of a colloid remain dispersed and do not settle due to gravity, and they are often electrically charged. Colloids are widespread in nature and are involved in many technological applications.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Identify the dispersed phase and the dispersion medium in each of the following colloidal systems: starch dispersion, smoke, fog, pearl, whipped cream, floating soap, jelly, milk, and ruby.

Solution:

Colloidal System	Dispersed Phase	Dispersion Medium
starch dispersion	starch	water
smoke	solid particles	air

Colloidal System	Dispersed Phase	Dispersion Medium
fog	water	air
pearl	water	calcium carbonate (CaCO ₃)
whipped cream	air	cream
floating soap	air	soap
jelly	fruit juice	pectin gel
milk	butterfat	water
ruby	chromium(III) oxide (Cr ₂ O ₃)	aluminum oxide (Al ₂ O ₃)

Exercise:

Problem:

Distinguish between dispersion methods and condensation methods for preparing colloidal systems.

Exercise:

Problem:

How do colloids differ from solutions with regard to dispersed particle size and homogeneity?

Solution:

Colloidal dispersions consist of particles that are much bigger than the solutes of typical solutions. Colloidal particles are either very large molecules or aggregates of smaller species that usually are big enough to scatter light. Colloids are homogeneous on a macroscopic (visual) scale, while solutions are homogeneous on a microscopic (molecular) scale.

Exercise:

Problem: Explain the cleansing action of soap.

Exercise:

Problem:

How can it be demonstrated that colloidal particles are electrically charged?

Solution:

If they are placed in an electrolytic cell, dispersed particles will move toward the electrode that carries a charge opposite to their own charge. At this electrode, the charged particles will be neutralized and will coagulate as a precipitate.

Glossary

amphiphilic

molecules possessing both hydrophobic (nonpolar) and a hydrophilic (polar) parts

colloid

(also, colloidal dispersion) mixture in which relatively large solid or liquid particles are dispersed uniformly throughout a gas, liquid, or solid

dispersion medium

solid, liquid, or gas in which colloidal particles are dispersed

dispersed phase

substance present as relatively large solid or liquid particles in a colloid

emulsifying agent

amphiphilic substance used to stabilize the particles of some emulsions

emulsion

colloid formed from immiscible liquids

gel




colloidal dispersion of a liquid in a solid

Tyndall effect
scattering of visible light by a colloidal dispersion

Period	Group																18			
1	1															2				
1	1 H 1.008 hydrogen															2 He 4.003 helium				
2	3 Li 6.94 lithium	4 Be 9.012 beryllium													5 B 10.81 boron	6 C 12.01 carbon	7 N 14.01 nitrogen	8 O 16.00 oxygen	9 F 19.00 fluorine	10 Ne 20.18 neon
3	11 Na 22.99 sodium	12 Mg 24.31 magnesium													13 Al 26.98 aluminum	14 Si 28.09 silicon	15 P 30.97 phosphorus	16 S 32.06 sulfur	17 Cl 35.45 chlorine	18 Ar 39.95 argon
4	19 K 39.10 potassium	20 Ca 40.08 calcium	21 Sc 44.96 scandium	22 Ti 47.87 titanium	23 V 50.94 vanadium	24 Cr 52.00 chromium	25 Mn 54.94 manganese	26 Fe 55.85 iron	27 Co 58.93 cobalt	28 Ni 58.69 nickel	29 Cu 63.55 copper	30 Zn 65.38 zinc	31 Ga 69.72 gallium	32 Ge 72.63 germanium	33 As 74.92 arsenic	34 Se 78.97 selenium	35 Br 79.90 bromine	36 Kr 83.80 krypton		
5	37 Rb 85.47 rubidium	38 Sr 87.62 strontium	39 Y 88.91 yttrium	40 Zr 91.22 zirconium	41 Nb 92.91 niobium	42 Mo 95.95 molybdenum	43 Tc [97] technetium	44 Ru 101.1 ruthenium	45 Rh 102.9 rhodium	46 Pd 106.4 palladium	47 Ag 107.9 silver	48 Cd 112.4 cadmium	49 In 114.8 indium	50 Sn 118.7 tin	51 Sb 121.8 antimony	52 Te 127.6 tellurium	53 I 126.9 iodine	54 Xe 131.3 xenon		
6	55 Cs 132.9 cesium	56 Ba 137.3 barium	57-71 La-Lu *	72 Hf 178.5 hafnium	73 Ta 180.9 tantalum	74 W 183.8 tungsten	75 Re 186.2 rhenium	76 Os 190.2 osmium	77 Ir 192.2 iridium	78 Pt 195.1 platinum	79 Au 197.0 gold	80 Hg 200.6 mercury	81 Tl 204.4 thallium	82 Pb 207.2 lead	83 Bi 209.0 bismuth	84 Po [209] polonium	85 At [210] astatine	86 Rn [222] radon		
7	87 Fr [223] francium	88 Ra [226] radium	89-103 Ac-Lr **	104 Rf [267] rutherfordium	105 Db [270] dubnium	106 Sg [271] seaborgium	107 Bh [270] bohrium	108 Hs [277] hassium	109 Mt [276] meitnerium	110 Ds [281] darmstadtium	111 Rg [282] roentgenium	112 Cn [285] copernicium	113 Uut [286] ununtrium	114 Fl [289] flerovium	115 Uup [288] ununpentium	116 Lv [293] livermorium	117 Uus [294] ununseptium	118 Uuo [294] ununoctium		
	57 La 138.9 lanthanum	58 Ce 140.1 cerium	59 Pr 140.9 praseodymium	60 Nd 144.2 neodymium	61 Pm [145] promethium	62 Sm 150.4 samarium	63 Eu 152.0 europium	64 Gd 157.3 gadolinium	65 Tb 158.9 terbium	66 Dy 162.5 dysprosium	67 Ho 164.9 holmium	68 Er 167.3 erbium	69 Tm 168.9 thulium	70 Yb 173.1 ytterbium	71 Lu 175.0 lutetium					
	89 Ac [227] actinium	90 Th 232.0 thorium	91 Pa 231.0 protactinium	92 U 238.0 uranium	93 Np [237] neptunium	94 Pu [244] plutonium	95 Am [243] americium	96 Cm [247] curium	97 Bk [247] berkelium	98 Cf [251] californium	99 Es [252] einsteinium	100 Fm [257] fermium	101 Md [258] mendelevium	102 No [259] nobelium	103 Lr [262] lawrencium					

The diagram shows a single element box from the periodic table for Hydrogen. The box is light blue with a thin black border. Inside the box, the atomic number '1' is at the top left, the symbol 'H' is in the center, the atomic mass '1.008' is below the symbol, and the name 'hydrogen' is at the bottom. Four labels with arrows point to these elements: 'Atomic number' points to '1', 'Symbol' points to 'H', 'Atomic mass' points to '1.008', and 'Name' points to 'hydrogen'.

Atomic number	1	Symbol	H
		Atomic mass	1.008
Name	hydrogen		

Color Code		
	Metal	Solid
	Metalloid	Liquid
	Nonmetal	Gas

Exponential Arithmetic

Exponential notation is used to express very large and very small numbers as a product of two numbers. The first number of the product, the *digit term*, is usually a number not less than 1 and not greater than 10. The second number of the product, the *exponential term*, is written as 10 with an exponent. Some examples of exponential notation are:

Equation:

$$\begin{aligned}1000 &= 1 \times 10^3 \\100 &= 1 \times 10^2 \\10 &= 1 \times 10^1 \\1 &= 1 \times 10^0 \\0.1 &= 1 \times 10^{-1} \\0.001 &= 1 \times 10^{-3} \\2386 &= 2.386 \times 1000 = 2.386 \times 10^3 \\0.123 &= 1.23 \times 0.1 = 1.23 \times 10^{-1}\end{aligned}$$

The power (exponent) of 10 is equal to the number of places the decimal is shifted to give the digit number. The exponential method is particularly useful notation for every large and very small numbers. For example, $1,230,000,000 = 1.23 \times 10^9$, and $0.00000000036 = 3.6 \times 10^{-10}$.

Addition of Exponentials

Convert all numbers to the same power of 10, add the digit terms of the numbers, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Example:

Adding Exponentials

Add 5.00×10^{-5} and 3.00×10^{-3} .

Solution

Equation:

$$\begin{aligned} 3.00 \times 10^{-3} &= 300 \times 10^{-5} \\ (5.00 \times 10^{-5}) + (300 \times 10^{-5}) &= 305 \times 10^{-5} = 3.05 \times 10^{-3} \end{aligned}$$

Subtraction of Exponentials

Convert all numbers to the same power of 10, take the difference of the digit terms, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Example:

Subtracting Exponentials

Subtract 4.0×10^{-7} from 5.0×10^{-6} .

Solution

Equation:

$$\begin{aligned} 4.0 \times 10^{-7} &= 0.40 \times 10^{-6} \\ (5.0 \times 10^{-6}) - (0.40 \times 10^{-6}) &= 4.6 \times 10^{-6} \end{aligned}$$

Multiplication of Exponentials

Multiply the digit terms in the usual way and add the exponents of the exponential terms.

Example:

Multiplying Exponentials

Multiply 4.2×10^{-8} by 2.0×10^3 .

Solution

Equation:

$$(4.2 \times 10^{-8}) \times (2.0 \times 10^3) = (4.2 \times 2.0) \times 10^{(-8)+(3)} = 8.4 \times 10^{-5}$$

Division of Exponentials

Divide the digit term of the numerator by the digit term of the denominator and subtract the exponents of the exponential terms.

Example:

Dividing Exponentials

Divide 3.6×10^5 by 6.0×10^{-4} .

Solution

Equation:

$$\frac{3.6 \times 10^5}{6.0 \times 10^{-4}} = \left(\frac{3.6}{6.0} \right) \times 10^{(5)-(-4)} = 0.60 \times 10^{-1} = 6.0 \times 10^{-2}$$

Squaring of Exponentials

Square the digit term in the usual way and multiply the exponent of the exponential term by 2.

Example:

Squaring Exponentials

Square the number 4.0×10^{-6} .

Solution

Equation:

$$(4.0 \times 10^{-6})^2 = 4 \times 4 \times 10^{2 \times (-6)} = 16 \times 10^{-12} = 1.6 \times 10^{-11}$$

Cubing of Exponentials

Cube the digit term in the usual way and multiply the exponent of the exponential term by 3.

Example:**Cubing Exponentials**

Cube the number 2×10^4 .

Solution**Equation:**

$$(2 \times 10^4)^3 = 2 \times 2 \times 2 \times 10^{3 \times 4} = 8 \times 10^{12}$$

Taking Square Roots of Exponentials

If necessary, decrease or increase the exponential term so that the power of 10 is evenly divisible by 2. Extract the square root of the digit term and divide the exponential term by 2.

Example:**Finding the Square Root of Exponentials**

Find the square root of 1.6×10^{-7} .

Solution**Equation:**

$$1.6 \times 10^{-7} = 16 \times 10^{-8}$$

$$\sqrt{16 \times 10^{-8}} = \sqrt{16} \times \sqrt{10^{-8}} = \sqrt{16} \times 10^{-\frac{8}{2}} = 4.0 \times 10^{-4}$$

Significant Figures

A beekeeper reports that he has 525,341 bees. The last three figures of the number are obviously inaccurate, for during the time the keeper was counting the bees, some of them died and others hatched; this makes it quite difficult to determine the exact number of bees. It would have been more accurate if the beekeeper had reported the number 525,000. In other words, the last three figures are not significant, except to set the position of the decimal point. Their exact values have no meaning useful in this situation. In reporting any information as numbers, use only as many significant figures as the accuracy of the measurement warrants.

The importance of significant figures lies in their application to fundamental computation. In addition and subtraction, the sum or difference should contain as many digits to the right of the decimal as that in the least certain of the numbers used in the computation (indicated by underscoring in the following example).

Example:

Addition and Subtraction with Significant Figures

Add 4.383 g and 0.0023 g.

Solution

Equation:

$$\begin{array}{r} 4.\underline{383} \text{ g} \\ 0.00\underline{23} \text{ g} \\ \hline 4.38\underline{5} \text{ g} \end{array}$$

In multiplication and division, the product or quotient should contain no more digits than that in the factor containing the least number of significant figures.

Example:

Multiplication and Division with Significant Figures

Multiply 0.6238 by 6.6.

Solution

Equation:

$$0.6238 \times 6.6 = 4.1$$

When rounding numbers, increase the retained digit by 1 if it is followed by a number larger than 5 (“round up”). Do not change the retained digit if the digits that follow are less than 5 (“round down”). If the retained digit is followed by 5, round up if the retained digit is odd, or round down if it is even (after rounding, the retained digit will thus always be even).

The Use of Logarithms and Exponential Numbers

The common logarithm of a number (log) is the power to which 10 must be raised to equal that number. For example, the common logarithm of 100 is 2, because 10 must be raised to the second power to equal 100. Additional examples follow.

Logarithms and Exponential Numbers		
Number	Number Expressed Exponentially	Common Logarithm

Logarithms and Exponential Numbers		
Number	Number Expressed Exponentially	Common Logarithm
1000	10^3	3
10	10^1	1
1	10^0	0
0.1	10^{-1}	-1
0.001	10^{-3}	-3

What is the common logarithm of 60? Because 60 lies between 10 and 100, which have logarithms of 1 and 2, respectively, the logarithm of 60 is 1.7782; that is,

Equation:

$$60 = 10^{1.7782}$$

The common logarithm of a number less than 1 has a negative value. The logarithm of 0.03918 is -1.4069, or

Equation:

$$0.03918 = 10^{-1.4069} = \frac{1}{10^{1.4069}}$$

To obtain the common logarithm of a number, use the *log* button on your calculator. To calculate a number from its logarithm, take the inverse log of the logarithm, or calculate 10^x (where x is the logarithm of the number).

The natural logarithm of a number (\ln) is the power to which e must be raised to equal the number; e is the constant 2.7182818. For example, the natural logarithm of 10 is 2.303; that is,

Equation:

$$10 = e^{2.303} = 2.7182818^{2.303}$$

To obtain the natural logarithm of a number, use the *ln* button on your calculator. To calculate a number from its natural logarithm, enter the natural logarithm and take the inverse ln of the natural logarithm, or calculate e^x (where x is the natural logarithm of the number).

Logarithms are exponents; thus, operations involving logarithms follow the same rules as operations involving exponents.

1. The logarithm of a product of two numbers is the sum of the logarithms of the two numbers.

Equation:

$$\log xy = \log x + \log y, \text{ and } \ln xy = \ln x + \ln y$$

2. The logarithm of the number resulting from the division of two numbers is the difference between the logarithms of the two numbers.

Equation:

$$\log \frac{x}{y} = \log x - \log y, \text{ and } \ln \frac{x}{y} = \ln x - \ln y$$

3. The logarithm of a number raised to an exponent is the product of the exponent and the logarithm of the number.

Equation:

$$\log x^n = n \log x \text{ and } \ln x^n = n \ln x$$

The Solution of Quadratic Equations

Mathematical functions of this form are known as second-order polynomials or, more commonly, quadratic functions.

Equation:

$$ax^2 + bx + c = 0$$

The solution or roots for any quadratic equation can be calculated using the following formula:

Equation:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Example:

Solving Quadratic Equations

Solve the quadratic equation $3x^2 + 13x - 10 = 0$.

Solution

Substituting the values $a = 3$, $b = 13$, $c = -10$ in the formula, we obtain

Equation:

$$x = \frac{-13 \pm \sqrt{(13)^2 - 4 \times 3 \times (-10)}}{2 \times 3}$$

Equation:

$$x = \frac{-13 \pm \sqrt{169 + 120}}{6} = \frac{-13 \pm \sqrt{289}}{6} = \frac{-13 \pm 17}{6}$$

The two roots are therefore

Equation:

$$x = \frac{-13 + 17}{6} = \frac{2}{3} \text{ and } x = \frac{-13 - 17}{6} = -5$$

Quadratic equations constructed on physical data always have real roots, and of these real roots, often only those having positive values are of any significance.

Two-Dimensional (x-y) Graphing

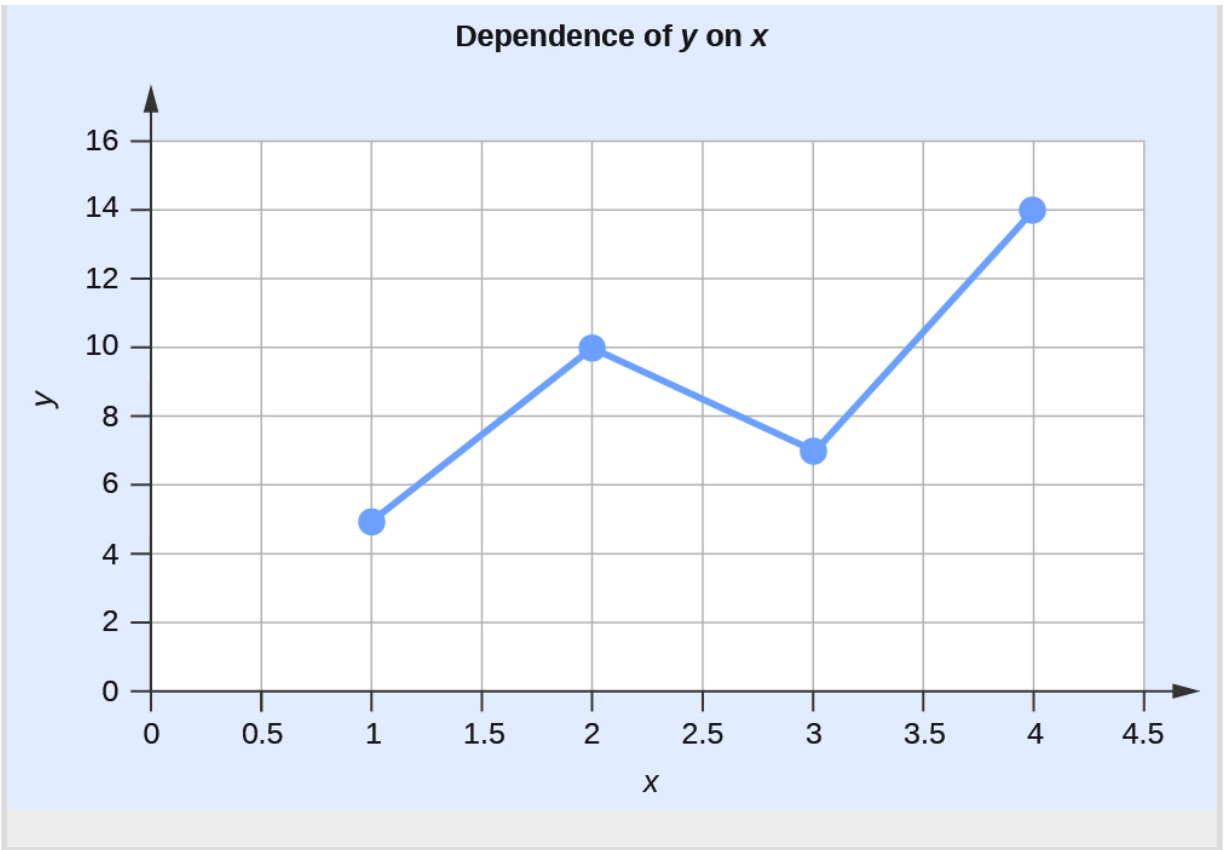
The relationship between any two properties of a system can be represented graphically by a two-dimensional data plot. Such a graph has two axes: a horizontal one corresponding to the independent variable, or the variable whose value is being controlled (x), and a vertical axis corresponding to the dependent variable, or the variable whose value is being observed or measured (y).

When the value of y is changing as a function of x (that is, different values of x correspond to different values of y), a graph of this change can be plotted or sketched. The graph can be produced by using specific values for (x,y) data pairs.

Example:
Graphing the Dependence of y on x

x	y
1	5
2	10
3	7
4	14

This table contains the following points: (1,5), (2,10), (3,7), and (4,14). Each of these points can be plotted on a graph and connected to produce a graphical representation of the dependence of y on x .



If the function that describes the dependence of y on x is known, it may be used to compute x, y data pairs that may subsequently be plotted.

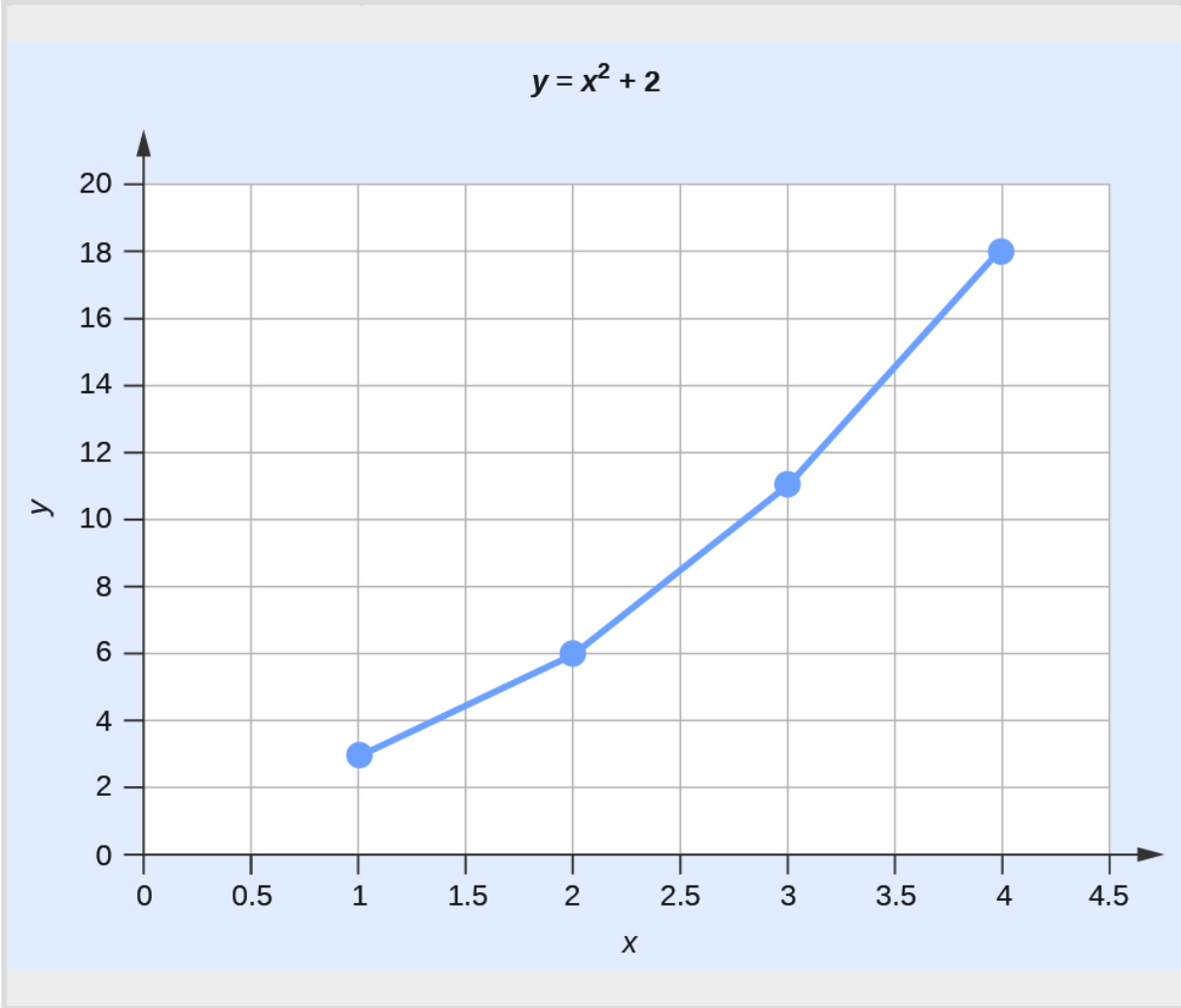
Example:

Plotting Data Pairs

If we know that $y = x^2 + 2$, we can produce a table of a few (x, y) values and then plot the line based on the data shown here.

x	$y = x^2 + 2$

x	$y = x^2 + 2$
1	3
2	6
3	11
4	18



Units and Conversion Factors

Units of Length			
meter (m)	= 39.37 inches (in.) = 1.094 yards (yd)	angstrom (Å)	= 10^{-8} cm (exact, definition) = 10^{-10} m (exact, definition)
centimeter (cm)	= 0.01 m (exact, definition)	yard (yd)	= 0.9144 m
millimeter (mm)	= 0.001 m (exact, definition)	inch (in.)	= 2.54 cm (exact, definition)
kilometer (km)	= 1000 m (exact, definition)	mile (US)	= 1.60934 km

Units of Volume

Units of Volume			
liter (L)	$= 0.001 \text{ m}^3$ (exact, definition) $= 1000 \text{ cm}^3$ (exact, definition) $= 1.057 \text{ (US) quarts}$	liquid quart (US)	$= 32 \text{ (US) liquid ounces (exact, definition)}$ $= 0.25 \text{ (US) gallon (exact, definition)}$ $= 0.9463 \text{ L}$
milliliter (mL)	$= 0.001 \text{ L}$ (exact, definition) $= 1 \text{ cm}^3$ (exact, definition)	dry quart	$= 1.1012 \text{ L}$
microliter (μL)	$= 10^{-6} \text{ L}$ (exact, definition) $= 10^{-3} \text{ cm}^3$ (exact, definition)	cubic foot (US)	$= 28.316 \text{ L}$

Units of Mass			
gram (g)	$= 0.001 \text{ kg}$ (exact, definition)	ounce (oz) (avoirdupois)	$= 28.35 \text{ g}$

Units of Mass			
milligram (mg)	= 0.001 g (exact, definition)	pound (lb) (avoirdupois)	= 0.4535924 kg
kilogram (kg)	= 1000 g (exact, definition) = 2.205 lb	ton (short)	=2000 lb (exact, definition) = 907.185 kg
ton (metric)	=1000 kg (exact, definition) = 2204.62 lb	ton (long)	= 2240 lb (exact, definition) = 1.016 metric ton

Units of Energy	
4.184 joule (J)	= 1 thermochemical calorie (cal)
1 thermochemical calorie (cal)	= 4.184×10^7 erg
erg	= 10^{-7} J (exact, definition)
electron-volt (eV)	= 1.60218×10^{-19} J = 23.061 kcal mol ⁻¹
liter·atmosphere	= 24.217 cal = 101.325 J (exact, definition)

Units of Energy	
nutritional calorie (Cal)	= 1000 cal (exact, definition) = 4184 J
British thermal unit (BTU)	= 1054.804 J [footnote] BTU is the amount of energy needed to heat one pound of water by one degree Fahrenheit. Therefore, the exact relationship of BTU to joules and other energy units depends on the temperature at which BTU is measured. 59 °F (15 °C) is the most widely used reference temperature for BTU definition in the United States. At this temperature, the conversion factor is the one provided in this table.

Units of Pressure	
torr	= 1 mm Hg (exact, definition)
pascal (Pa)	= N m ⁻² (exact, definition) = kg m ⁻¹ s ⁻² (exact, definition)
atmosphere (atm)	= 760 mm Hg (exact, definition) = 760 torr (exact, definition) = 101,325 N m ⁻² (exact, definition) = 101,325 Pa (exact, definition)
bar	= 10 ⁵ Pa (exact, definition) = 10 ⁵ kg m ⁻¹ s ⁻² (exact, definition)

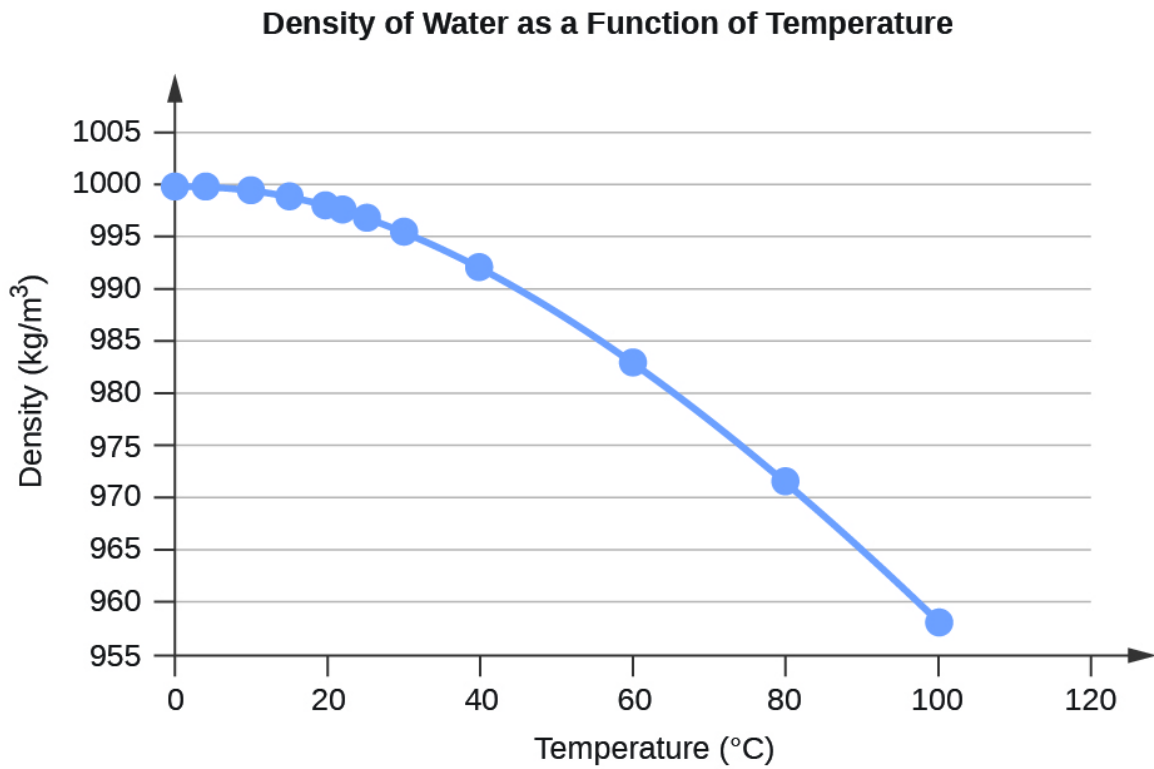
Fundamental Physical Constants

Fundamental Physical Constants	
Name and Symbol	Value
atomic mass unit (amu)	$1.6605402 \times 10^{-27} \text{ kg}$
Avogadro's number	$6.0221367 \times 10^{23} \text{ mol}^{-1}$
Boltzmann's constant (k)	$1.380658 \times 10^{-23} \text{ J K}^{-1}$
charge-to-mass ratio for electron (e/m_e)	$1.75881962 \times 10^{11} \text{ C kg}^{-1}$
electron charge (e)	$1.60217733 \times 10^{-19} \text{ C}$
electron rest mass (m_e)	$9.1093897 \times 10^{-31} \text{ kg}$
Faraday's constant (F)	$9.6485309 \times 10^4 \text{ C mol}^{-1}$
gas constant (R)	$8.205784 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1} = 8.314510 \text{ J mol}^{-1} \text{ K}^{-1}$
molar volume of an ideal gas, 1 atm, 0 °C	$22.41409 \text{ L mol}^{-1}$
molar volume of an ideal gas, 1 bar, 0 °C	$22.71108 \text{ L mol}^{-1}$
neutron rest mass (m_n)	$1.6749274 \times 10^{-27} \text{ kg}$

Fundamental Physical Constants	
Name and Symbol	Value
Planck's constant (h)	$6.6260755 \times 10^{-34} \text{ J s}$
proton rest mass (m_p)	$1.6726231 \times 10^{-27} \text{ kg}$
Rydberg constant (R)	$1.0973731534 \times 10^7 \text{ m}^{-1} =$ $2.1798736 \times 10^{-18} \text{ J}$
speed of light (in vacuum) (c)	$2.99792458 \times 10^8 \text{ m s}^{-1}$

Water Properties

Water Density (kg/m ³) at Different Temperatures (°C)	
Temperature ^{footnote} Data for t < 0 °C are for supercooled water	Density
0	999.8395
4	999.9720 (density maximum)
10	999.7026
15	999.1026
20	998.2071
22	997.7735
25	997.0479
30	995.6502
40	992.2
60	983.2
80	971.8
100	958.4

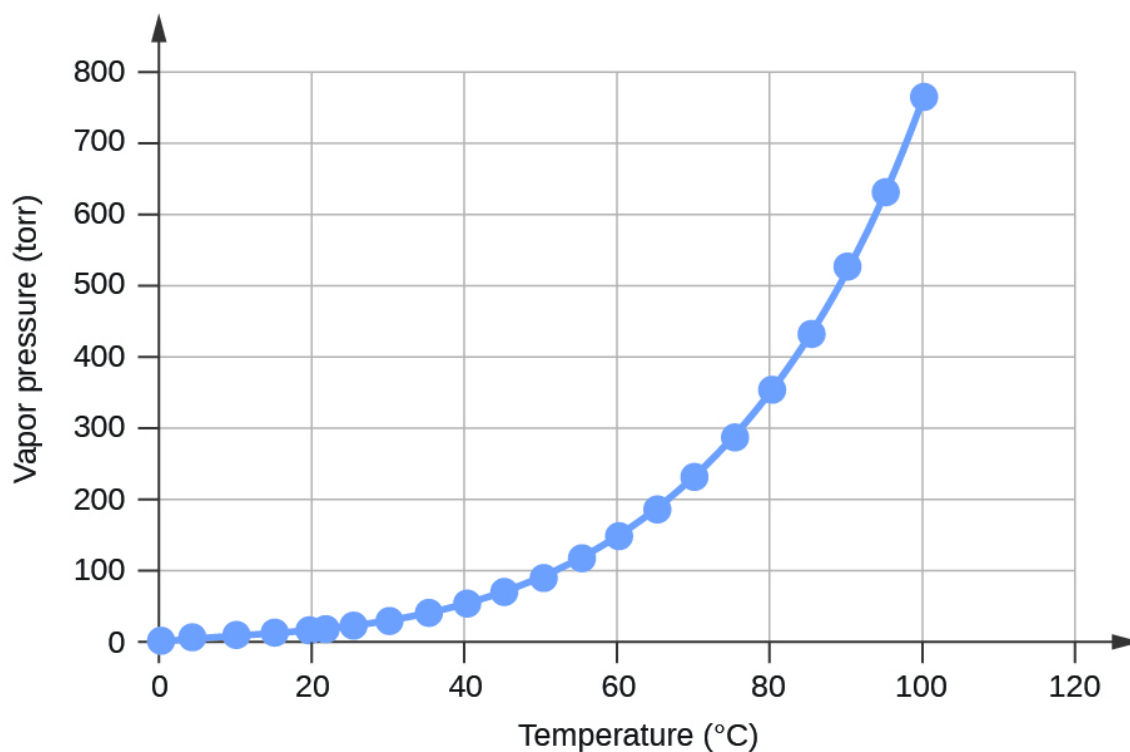


Water Vapor Pressure at Different Temperatures (°C)		
Temperature	Vapor Pressure (torr)	Vapor Pressure (Pa)
0	4.6	613.2812
4	6.1	813.2642
10	9.2	1226.562
15	12.8	1706.522

Water Vapor Pressure at Different Temperatures (°C)		
Temperature	Vapor Pressure (torr)	Vapor Pressure (Pa)
20	17.5	2333.135
22	19.8	2639.776
25	23.8	3173.064
30	31.8	4239.64
35	42.2	5626.188
40	55.3	7372.707
45	71.9	9585.852
50	92.5	12332.29
55	118.0	15732
60	149.4	19918.31
65	187.5	24997.88
70	233.7	31157.35
75	289.1	38543.39
80	355.1	47342.64
85	433.6	57808.42
90	525.8	70100.71

Water Vapor Pressure at Different Temperatures (°C)		
Temperature	Vapor Pressure (torr)	Vapor Pressure (Pa)
95	633.9	84512.82
100	760.0	101324.7

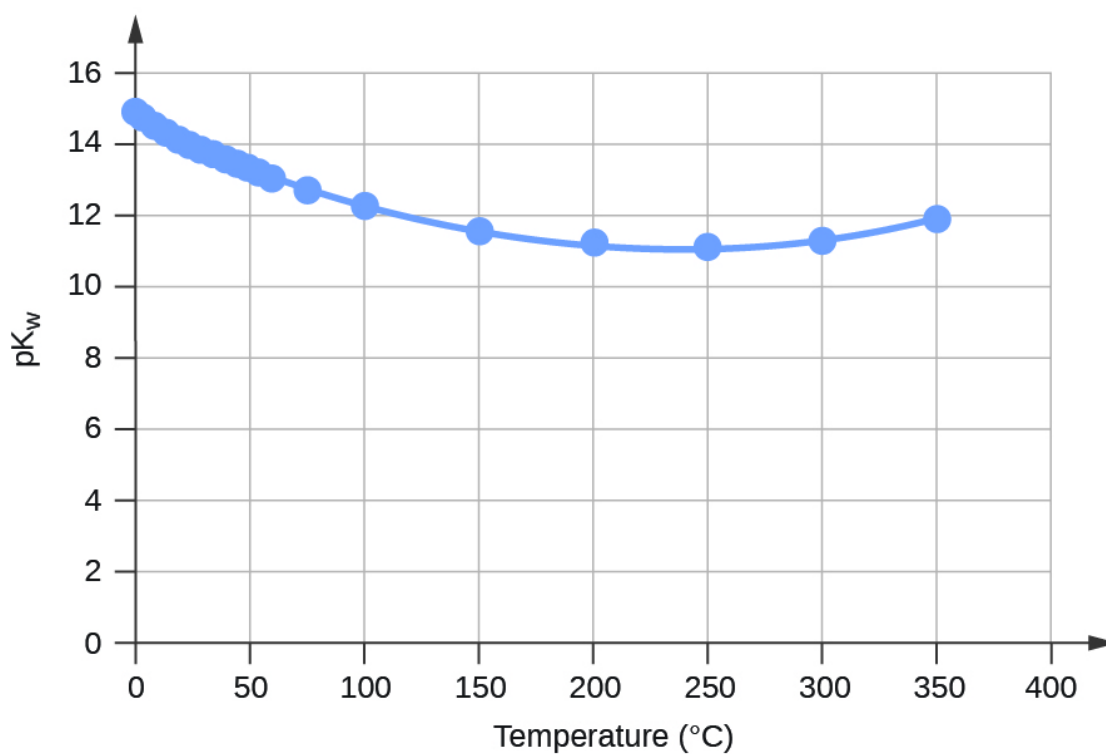
Vapor Pressure as a Function of Temperature



Water K_w and pK_w at Different Temperatures (°C)

Water K_w and pK_w at Different Temperatures (°C)		
Temperature	$K_w \cdot 10^{-14}$	$pK_w = -\log_{10}(K_w)$
Temperature	$K_w \cdot 10^{-14}$	pK_w $pK_w = -\log_{10}(K_w)$
0	0.112	14.95
5	0.182	14.74
10	0.288	14.54
15	0.465	14.33
20	0.671	14.17
25	0.991	14.00
30	1.432	13.84
35	2.042	13.69
40	2.851	13.55
45	3.917	13.41
50	5.297	13.28
55	7.080	13.15
60	9.311	13.03
75	19.95	12.70
100	56.23	12.25

Water pK_w as a Function of Temperature



Specific Heat Capacity for Water

$$C^\circ(\text{H}_2\text{O}(l)) = 4184 \text{ J}\cdot\text{K}^{-1}\cdot\text{kg}^{-1} = 4.184 \text{ J}\cdot\text{g}^{-1}\cdot^\circ\text{C}^{-1}$$

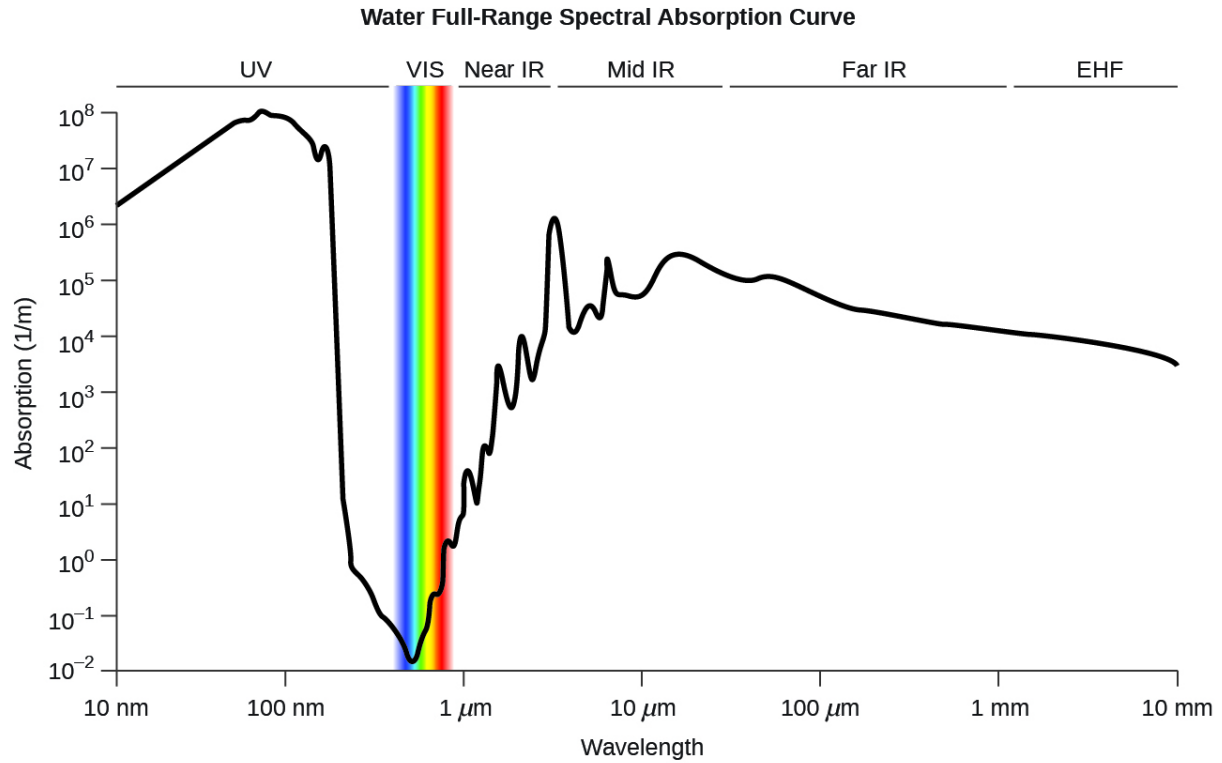
$$C^\circ(\text{H}_2\text{O}(s)) = 1864 \text{ J}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}$$

$$C^\circ(\text{H}_2\text{O}(g)) = 2093 \text{ J}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}$$

Standard Water Melting and Boiling Temperatures and Enthalpies of the Transitions		
	Temperature (K)	ΔH (kJ/mol)
melting	273.15	6.088
boiling	373.15	40.656 (44.016 at 298 K)

	Temperature (K)	ΔH (kJ/mol)
melting	273.15	6.088
boiling	373.15	40.656 (44.016 at 298 K)

Water Cryoscopic (Freezing Point Depression) and Ebullioscopic (Boiling Point Elevation) Constants
$K_f = 1.86^{\circ}\text{C}\cdot\text{kg}\cdot\text{mol}^{-1}$ (cryoscopic constant)
$K_b = 0.51^{\circ}\text{C}\cdot\text{kg}\cdot\text{mol}^{-1}$ (ebullioscopic constant)



Water full-range spectral absorption curve. This curve shows the full-range spectral absorption for water. The y-axis signifies the absorption in 1/cm. If we divide 1 by this value, we will obtain the length of the path (in cm) after which the intensity of a light beam passing through water decays by a factor of the base of the natural logarithm e ($e = 2.718281828$).

Composition of Commercial Acids and Bases

Composition of Commercial Acids and Bases			
Acid or Base[footnote] Acids and bases are commercially available as aqueous solutions. This table lists properties (densities and concentrations) of common acid and base solutions. Nominal values are provided in cases where the manufacturer cites a range of concentrations and densities.	Density (g/mL) [footnote] This column contains specific gravity data. In the case of this table, specific gravity is the ratio of density of a substance to the density of pure water at the same conditions. Specific gravity is often cited on commercial labels.	Percentage by Mass	Molarity
acetic acid, glacial	1.05	99.5%	17.4

aqueous ammonia [footnote] This solution is sometimes called “ammonium hydroxide,” although this term is not chemically accurate.	0.90	28%	14.8
hydrochloric acid	1.18	36%	11.6
nitric acid	1.42	71%	16.0
perchloric acid	1.67	70%	11.65
phosphoric acid	1.70	85%	14.7
sodium hydroxide	1.53	50%	19.1
sulfuric acid	1.84	96%	18.0